Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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

Yuanyuan Zhou, Hui Tang, Peiyi Wu**

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science and Laboratory for Advanced Materials, Fudan University, Shanghai 200433, China.

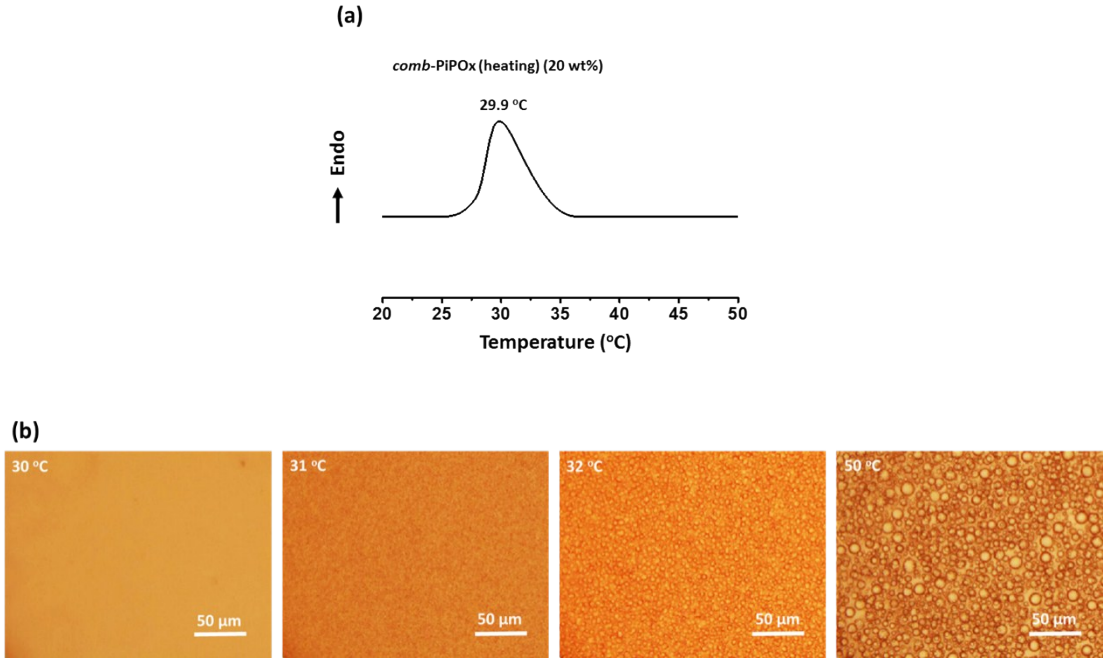

Figure S1. (a) DSC curve and (b) optical micrographs of comb-PiPOx aqueous solution (20 wt%) at different temperatures during the LLPS processes.

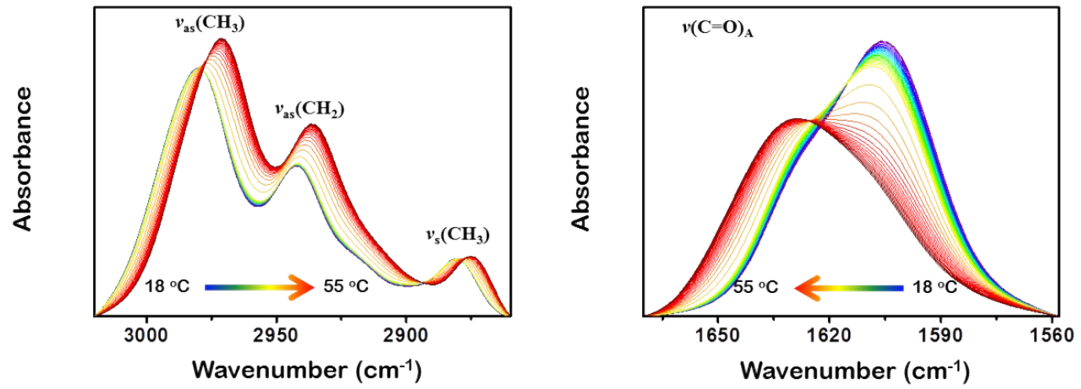

Figure S2. Variable-temperature FTIR spectra of linear-PiPOx in D2O (5 wt%) upon heating from 18 to 55 oC with an interval of 1 oC in the spectral regions 3020-2860 and 1670-1560 cm-1.

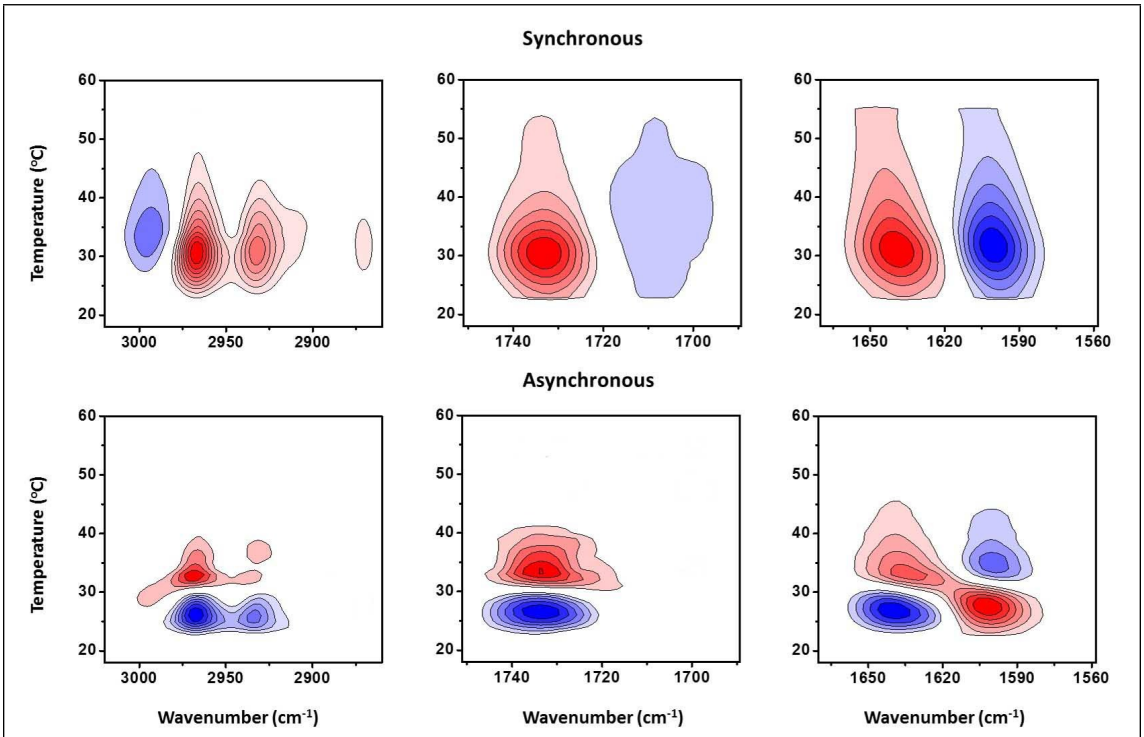

Figure S3. PCMW synchronous and asynchronous spectra of comb-PiPOx in D2O (5 wt%). Warm colors (red) are defined as positive intensities and cool colors (blue) are defined as negative intensities.

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_2CH_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_2CH_2-N)$_n$-CH_3 side chain of POiPOxMA is fairly similar to the (O-CH_2CH_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 (ν_1, ν_2) ($\nu_1 > \nu_2$) have the same symbol (both positive or both negative), the vibration mode at ν_1 takes places earlier response to external perturbation than the one at ν_2; otherwise, if the two cross-correlation peaks exhibit opposite symbol (one positive and the other one negative), the vibration mode at ν_1 takes place later response to external perturbation than the one at ν_2.

1. Y. Katsumoto, A. Tsuchiizu, X. Qiu and F. M. Winnik, *Macromolecules*, 2012, **45**, 3531-3541.

2. T. Li, H. Tang and P. Wu, *Langmuir*, 2015, **31**, 6870-6878.
3. T. Li, H. Tang and P. Wu, *Soft Matter*, 2015, **11**, 1911-1918.
4. C. Weber, C. R. Becer, R. Hoogenboom and U. S. Schubert, *Macromolecules*, 2009, **42**, 2965-2971.
5. Y. Maeda, T. Kubota, H. Yamauchi, T. Nakaji and H. Kitano, *Langmuir*, 2007, **23**, 11259-11265.
6. Y. Maeda, H. Yamauchi and T. Kubota, *Langmuir*, 2009, **25**, 479-482.
7. S. Sun and P. Wu, *Macromolecules*, 2013, **46**, 236-246.
8. B. Zhang, H. Tang and P. Wu, *Macromolecules*, 2014, **47**, 4728-4737.
9. Y. Zhou, H. Tang and P. Wu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 25525-25535.