Freeze-Thaw-Induced Mesoscale Reorganization in Gel-Gel Phase-Separated PEG Hydrogels

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Background and objective:

Gel-gel phase separation (GGPS) in dilute tetra-PEG networks produces co-continuous PEG-rich and PEG-poor gel phases within a single covalently crosslinked network [1,2]. We investigated how a single freeze-thaw cycle reorganizes this phase-separated structure and whether the response differs from that of a homogeneous gel prepared above the overlap concentration (c*). Stoichiometric tetra-PEG hydrogels were prepared at 10 g L^{-1} (GGPS gel) and 80 g L^{-1} (c* gel). Each gel was measured before and after freezing at -20 °C for 24 h and thawing at 25 °C for 24 h.

Results.:

Before freeze-thaw processing, the GGPS gel exhibited a pronounced intensity upturn toward low q (**Fig. 1**). This enhancement indicates long-wavelength polymer-density correlations and is consistent with concentration fluctuations between the co-continuous PEG-rich and PEG-poor gel phases. In contrast, the c* gel showed no comparable low-q upturn, in agreement with its homogeneous network. After freeze-thaw processing, the low-q intensity of the GGPS gel was strongly suppressed, demonstrating attenuation or reorganization of the pre-existing mesoscale concentration contrast.

Discussion and conclusion:

Combined with confocal observations of approximately 100 µm interconnected pores, the scattering change is consistent with expansion of the PEG-poor pathway during freezing and densification of the PEG-rich skeleton. SANS does not directly resolve the macropores; it detects the accompanying reorganization of polymer-density correlations over its accessible length scale. The c* gel profiles remained nearly unchanged, showing that ice formation alone does not generate this transition in a homogeneous network. Thus, GGPS pre-encodes a mesoscale topology that is selectively developed by freeze-thawing, providing scattering evidence for a phase-templating route to stable, percolating PEG sponges.

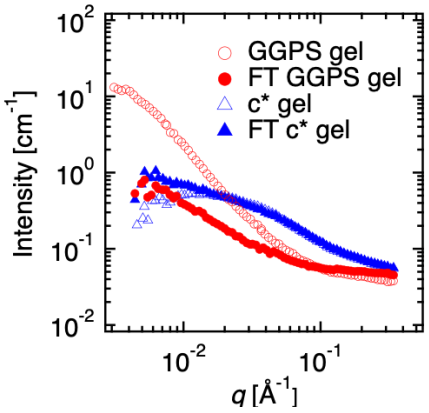

Fig. 1. SANS profiles of 10 g L^{-1} GGPS and 80 g L^{-1} c* gels before (open) and after (filled) freeze-thawing.

[1] S. Ishikawa et al., Nat. Mater. 22, 1564-1570 (2023).
[2] S. Ishikawa et al., ACS Macro Lett. 13, 1369-1375 (2024).