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**Probing the Influence of the Assembly of Polymer Additives in the Reinforcement of Responsive Gels**

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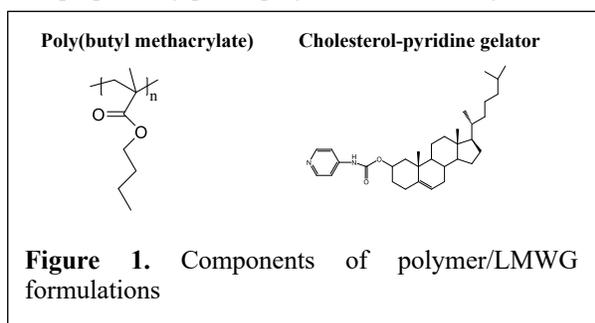
Responsive or “smart gels” have emerged as a flexible material platform for technologies ranging from sensors and dental composites to membranes and polymer actuators. The incorporation of polymer additives in low molecular weight gel (LMWG) formulations has been suggested to offer a robust, technologically-relevant method toward tunability in gel structure and responsiveness, polymer organization, and enhanced function. We are motivated to elucidate the synergistic organization of the gel components as a function of the mode of incorporation of the polymer filler and to establish key factors connecting this gel assembly, rheological behavior, and responsiveness. The goals of this New Directions Proposal are to investigate systematically the resultant gel properties when polymers are introduced via the following methods: (1) *solubilized monomer that is polymerized post-LMWG gelation*, (2) *pre-formed polymer solubilized prior to LMWG gelation*, and (3) *a preformed supramolecular polymer whose functionality is engaged pre- and post-gelation by the LMWG*.

During the second funding year and inspired by prior studies of nucleation effects of polymer additives in LMWG formulations, we focused on the influence of polymer-reinforcement pre- and post-gelation. The post-doc, graduate, and undergraduate students involved formed a strong research team, emphasizing mentoring and leadership in addition to fundamental exposure to polymer and small molecule synthesis and characterization techniques.

*1. Design and preparation of LMWG-polymer composite networks*

1.1. Polymer inclusion after gelation

To realize the introduction of polymers in the LMWG network, the LMWG-polymer composite networks (Gel-A) were prepared by photo-polymerization of butyl methacrylate (BMA) in CP gels at the temperature below the sol-gel



transition temperature ( $T_{\text{sol-gel}}$ ) of CP gel (**Figure 1**). Specifically, CP gelators were dissolved in BMA/anisole (35/65) at 90 °C. After adding photo-initiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) which was 1/1000 equivalent to BMA, the gelator solution was quickly cooled down to room temperature for the gelation of CP gelators. The photo-polymerization of BMA was achieved under 11.2 mW/cm<sup>2</sup> UV radiation (356 nm) for 1 h. During the polymerization, the temperature of gel system was kept lower than 40 °C to ensure the LMWG network structure was preserved.

1.2. Polymer inclusion before gelation

To compare the structure and mechanical properties of composite gel with different methods of polymer inclusion, a control polymer-LMWG composite network (Gel-B) was prepared by introducing preformed PBMA to the CP gel in prior to the gelation. Poly(butyl methacrylate) (PBMA) was first synthesized with same BAPO/BMA/anisole ratio, UV irradiation conditions, reaction time and temperature as used for Gel-A preparation. The CP gelator was then to the PBMA solution. The BMA/anisole solution (35/65) was purged with nitrogen gas for 15 min before adding the BAPO. The reaction solution was placed 11.2 mW/cm<sup>2</sup> UV radiation (356 nm) for 1 h with temperature below 40 °C. The CP gelator was dissolved in reaction solution without further purification. After cooling down to room temperature, Gel-B was formed.

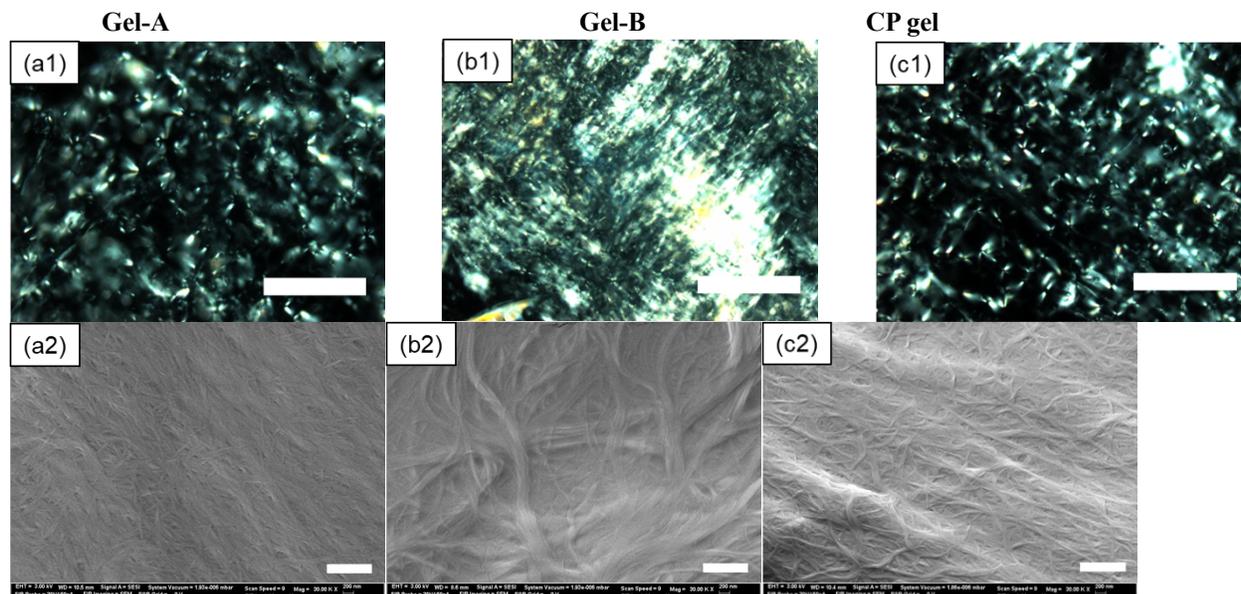
*2. Characterization*

2.1. Gel components

The PBMA in Gel-A and Gel-B were both high molecular weight (~250 kg/mol) and similar dispersity (~3). Based on <sup>1</sup>H-NMR data, we confirmed that Gel-A and Gel-B consisted of the same concentration of PBMA (7.3 wt%) and CP gelator (3.2 wt%). This is critical to the investigation of the effect of polymer inclusion method on LMWG properties, because it well-known that changes in the gelation solvent and polymer concentration can result in variations in the LMWG structure.<sup>2</sup>

## 2.2. Structures of gels

The structures of Gel-A, Gel-B and CP gel in the wet and dry state were investigated using polarized optical microscopy (POM) and scanning electron microscopy (SEM), respectively (**Figure 2**). Spherulites with similar size were observed in the images (a1- Gel A and c1- Gel B) (**Figure 2**), suggesting the unchanged LMWG structure in network-level after polymer inclusion. In contrast, the LMWG structure of Gel-B was dramatically different, exhibiting a disappearance of the spherulitic structure, but the emergence of a single fiber network shown (**Figure 2** b1). These observations suggest that the introduction of PBMA after the gelation of CP did not cause a variation in the LMWG structure. However, addition of PBMA prior to gelation affected the self-assembly behavior of CP, hence changing the LMWG morphology. SEM studies (**Figure 2: a2-c2**) support these conclusions, highlighting the presence of thicker fiber bundles likely due to the adsorption of PBMA chains along the surface of CP fibers similar to our previous work.<sup>3</sup>



**Figure 2.** (a1-c1) are POM images of wet gels, and (a2-c2) are SEM images of dried gels. The polymer-LMWG composite gels were fabricated by introducing PBMA into the CP gel before (b1-2) and after (a1-2) gelation. (c1-2) are images of the pure CP gel. The lengths of the scale bar in (a1-c1) and (a2-c2) are 0.5 mm and 600 nm, respectively.

The CP gelator assembly modes in Gel-A, Gel-B and CP gel at wet state were studied through small-angle X-ray scattering (SAXS), revealing a  $q$  spacing order of 1:2:3, which indicates a lamellar CP structure regardless of mode of fabrication.

## 2.3. Mechanical properties of gels

In the future, the rheological response of Gel-A, Gel-B and CP gel will be investigated. We expect Gel-A has highest strength and elasticity with excellent recovery.<sup>4,5</sup> We will explore these systems for three-dimensional printing applications. Responsive (photo- and thermo-) properties are also under exploration.

## References

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