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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 first funding year and inspired by prior studies of nucleation effects of polymer additives in LMWG formulations, we focused on three main objectives: 1) exploring rheological and microstructural changes as a function of LMWG gel concentration with pre-formed polymer, 2) in situ synthesis of solubilized polymer post-LMWG gelation, and 3) design and synthesis of a fluorescent LMWG for in situ visualization of gelation.

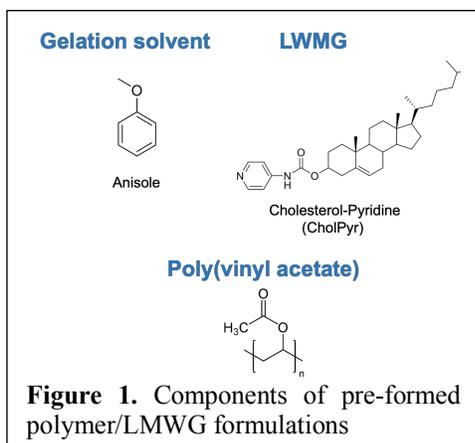


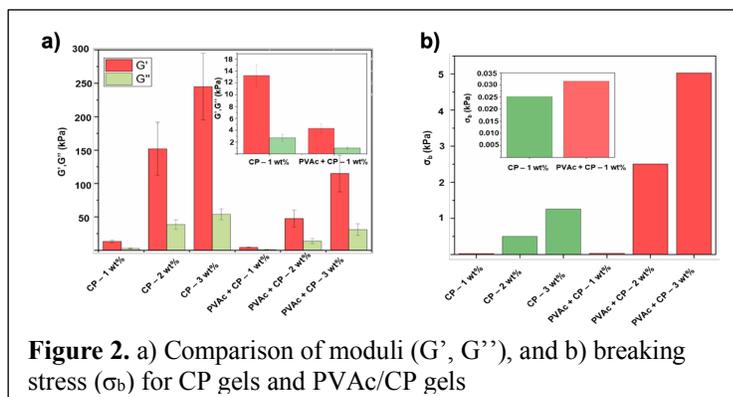
Figure 1. Components of pre-formed polymer/LMWG formulations

1) Rheological and microstructural investigation in pre-formed/LMWG formulations Initial studies have focused on the cholesterol pyridine (CP) LMWG, given our previous studies on this system, poly(vinyl acetate) (PVAc), and anisole (**Figure 1**). A cholesterol-pyridine (CP) gelator was synthesized using cholesterol chloroformate and 4-aminopyridine, which has been described in our previous work.¹ This approach allowed us to focus on the fundamentals of assembly in parallel to fluorescent gelator design.

The concentration of CP gelator in anisole for the formulations were varied at 1, 2 and 3 wt%. The concentration of PVAc solution was kept constant at 50 mg/ml. The PVAc/anisole/CP formulations were stirred at 100 °C until complete dissolution. Using the vial inversion method, the solution was cooled to room temperature until loss of solvent flow.

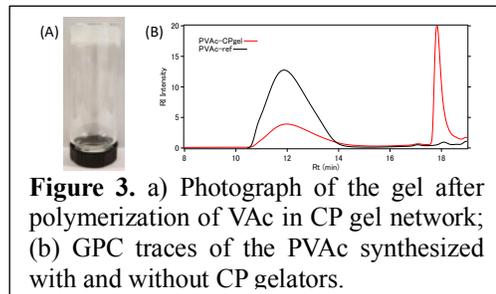
Rheological studies of the CP gel/anisole and PVAc/anisole/CP formulations indicate that PVAc + CP gels display comparatively weaker mechanical behavior compared to that of neat CP gels (**Figure 2a**). This trend is observed in gels with polymer additives which adsorb strongly on the surface of the fibers.² The difference in the rheological behavior of both the systems is indicative of structural changes in the gel network, which will be further studied via small-angle neutron scattering (SANS) and confocal microscopy with a fluorescent gelator. An additional measure of gel strength is the breaking stress (σ_b) (**Figure 2b**), which represents the force necessary to disrupt the mechanical integrity of the gel network completely. Gels prepared in the presence of PVAc exhibited significantly larger breaking stress as compared to that of neat CP gels beyond 1 wt% CP concentration.

2) In situ synthesis of solubilized PVAc post-LMWG gelation Radical polymerization of the vinyl acetate (VAc) in CP gel network was achieved using UV initiation (**Figure 3a**), at a wavelength of 365 nm, with phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) as the photoinitiator. Specifically, 125.5 mg of CP gelator was dissolved in 3.28 mL of anisole at 90 °C in a 40 ml

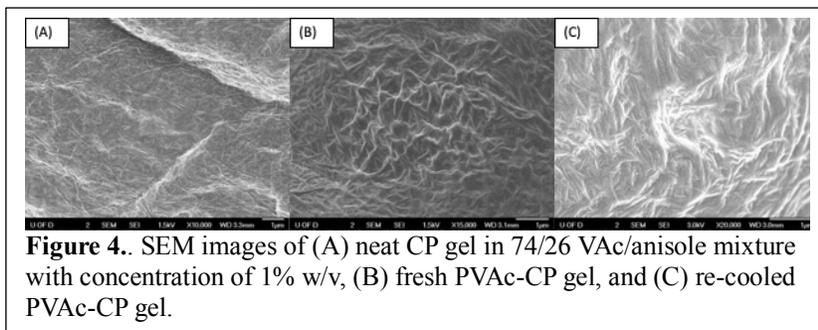


The molecular weight (MW) and dispersity (\mathcal{D}) of PVAc were measured by gel permeation chromatography (GPC) with tetrahydrofuran as the mobile phase. Both polymerization, with CP gelator (PVAc-CP gel) and without CP gelators (PVAc-ref), yield PVAc with high MW ($M_n^{\text{PVAc-CPgel}} = 70$ kDa, $M_n^{\text{PVAc-ref}} = 81$ kDa), as shown in **Figure 3b**. The concentration of PVAc in the CP gel was 2.2 mg/ml, determined by ^1H NMR.

vial. To that solution, then 9.22 mL of VAc and 4.9 mg BAPO were added. After cooling the reaction mixture to 0°C to form the gel, the vial was placed under 6.7 mW/cm^2 UV radiation for 1 h. The CP gelator concentration was 1% (w/v) and the ratio of VAc and anisole was 74/26. The entire procedure was conducted under nitrogen atmosphere. Poly(vinyl acetate) (PVAc) was synthesized as a reference using similar reaction conditions, but without adding CP gelator.



Scanning electron microscopy (SEM) was used to examine the morphology of the dried PVAc/CP gel network. Before the SEM measurement, all the samples were dried in vacuum at room temperature overnight and then sputter-coated Au/Pd layer. To examine the impact of reformation, a PVAc-CP gel was also prepared by heating fresh PVAc-CP gel and followed re-cooling. **Figure 4a** highlights the formation of highly connected, fibrillar structure of the CP gelator within the *in situ* formed PVAc. The same structure has also been observed by our group as CP gel in pure anisole.¹ In **Figure 4b,c**, both of the fresh and re-cooled PVAc-CP gels exhibited nanofiber structures of similar diameter, but the fibers in the freshly PVAc-CP formulation were much more cross-winding, exhibiting woven-textile-like structure.



It is proposed that the interaction of PVAc polymer chains and CP fibers drives the fibrillar organization. For the fresh PVAc-CP gel, polymerization occurred in pre-formed CP gel network, templating polymer growth along the CP network structure. After heating, the CP was disrupted; upon reformation of the CP network, the fibers grew along the existing entangled PVAc chains, impacting length and interconnectivity.

We expect that the fresh PVAc-CP gel will higher mechanical properties than the re-cooling one, which will be examined via rheology.

3) Fluorescent gelator synthesis The synthesis of benzoxazole-based gelator was attempted.³⁻⁵ However, the low sol-gel transition and minimal gelation solvent versatility suggest that another gelator is needed. We are currently focused on a naphthalimide-based gelator derived from CP for other studies that may address the current challenges.

References 1. Alexander, S. L. M.; Korley, L. T. J. *Polym J* **2018**, 50, (8), 775; 2. J. L. Li, B. Yuan, X. Y. Liu, X. G. Wang, and R. Y. Wang, "Kinetically controlled homogenization and transformation of crystalline fiber networks in supramolecular materials," *Cryst. Growth Des.*, vol. 11, no. 7, pp. 3227, 2011; 3) Kim, T. H.; Choi, M. S.; Sohn, B. H.; Park, S. Y.; Lyoo, W. S.; Lee, T. S. *Chem Commun* **2008**, (20), 2364; 4) Srikun, D.; Miller, E. W.; Dornaille, D. W.; Chang, C. J. *J Am Chem Soc* **2008**, 130, (14), 4596; 5) Zhang, X.; Li, H. M.; Mu, H. F.; Liu, Y. F.; Guan, Y. A.; Yoon, J.; Yu, H. T. *Dyes and Pigments* **2017**, 147, 40-49.