Effect of Allylation on Gelation Behavior of Aqueous Methylcellulose Solutions

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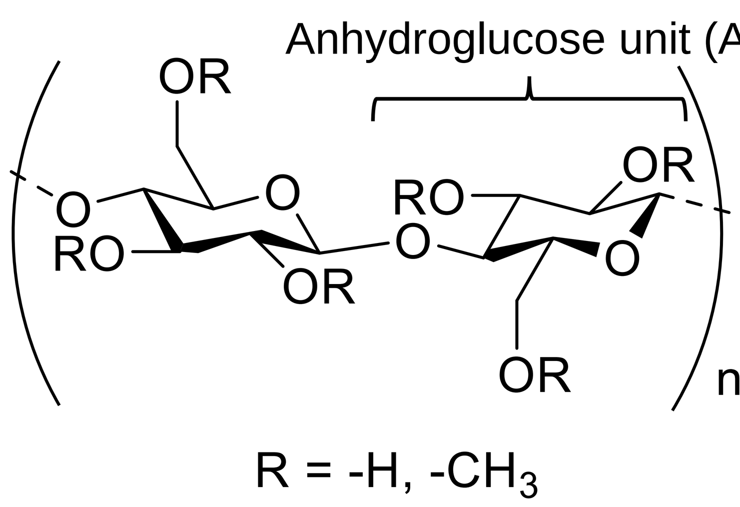
Jerrick Edmund, McKenzie L. Coughlin, Timothy P. Lodge and Frank S. Bates
Department of Chemical Engineering and Materials Science

UROP Undergraduate Research Opportunities Program

Background

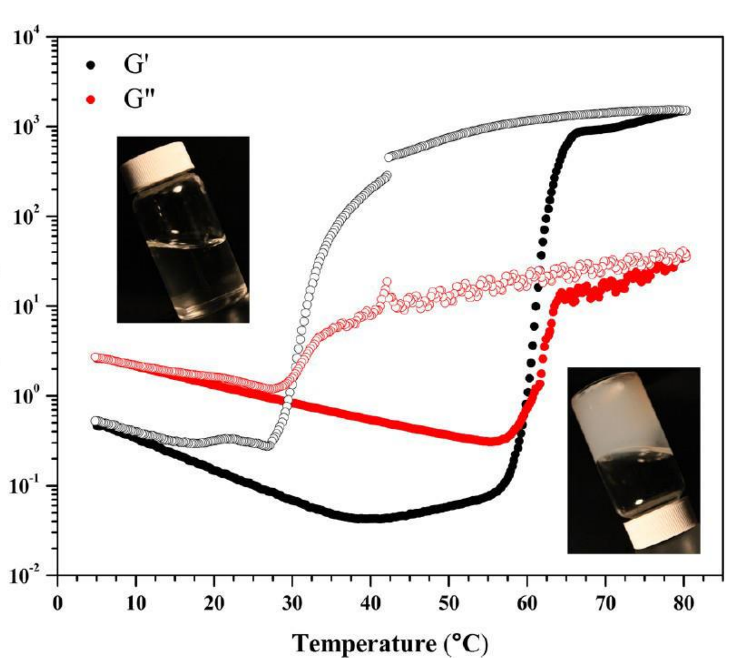


Methylcellulose (MC) is a water-soluble cellulose ether formed by the partial substitution of hydroxyl groups with methoxy moieties. MC becomes hydrophobic outside the DS range of 1.6-2.1.

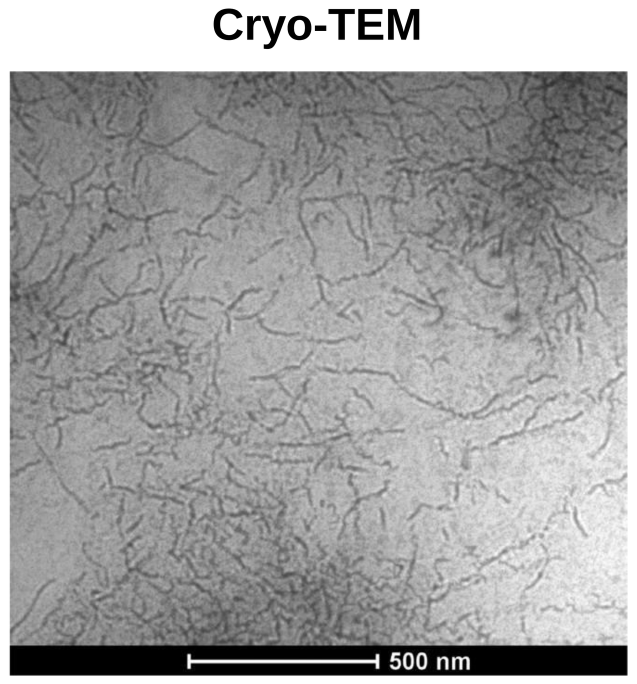
Methylcellulose has many real-life applications due to its thickening and emulsifying properties, including:

MC is a thermoreversible gel that is water-soluble at low temperatures and phase separates and gels at ~60 °C. Cryogenic transmission electron microscopy (cryo-TEM) images show that fibrils of diameter 15 ± 2 nm form when gelation occurs.

Rheology



Cryo-TEM

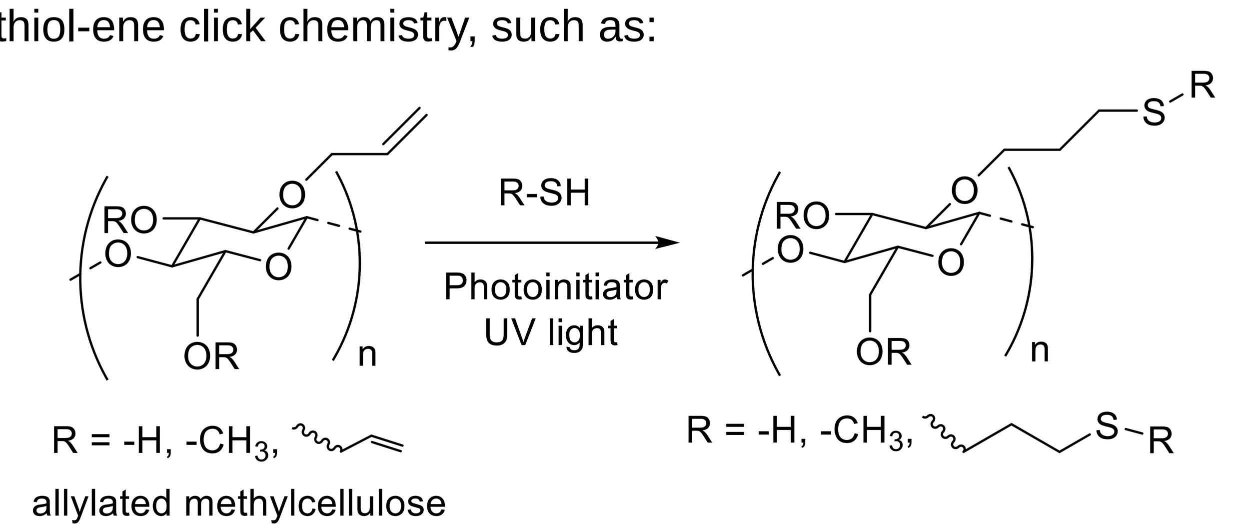


Lott, J. R. et al. *Biomacromolecules*. **2013**, *14*, 2484-2488.

Objective and Motivation

The objective of this project is to understand the change in gelation behavior of MC solutions substituted with allyl groups.

Allylated MCs can be used to design synthesis routes for polymer grafting through thiol-ene click chemistry, such as:



Experimental Methods

Materials
METHOCEL A4C of molecular weight (M_w) 150 kg/mol, allyl bromide, 1 M aqueous sodium hydroxide (NaOH(aq)) and water

Synthesis
~500 mg MC was dissolved in 30 mL of 1 M NaOH(aq). Desired amounts of allyl bromide were added, ranging from 100-800 µL. Solutions were stirred at room temperature for 16 hours, subsequently dialyzed against water for 1 day. Final products were isolated via freeze-drying.

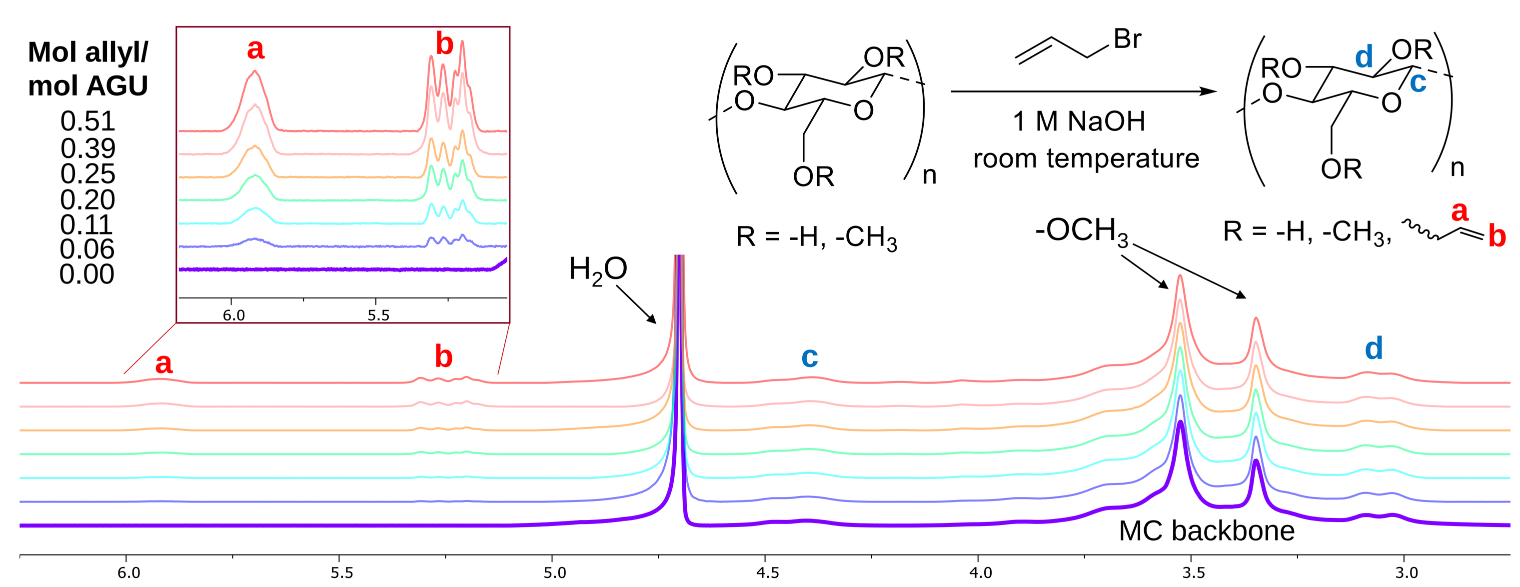
Characterization
Degree of allylation was characterized using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy.

Optical Transmittance
- 0.5 mL of 2 wt% solutions used
- Heating rate = 2.5 °C/min from 20 to 80 °C
- The cloud point (T_{cloud}) is when the solution starts to become turbid and is often used to locate the phase boundary
- T_{cloud} was determined from 0.86 relative transmittance of a 633 nm laser source on the solution

Rheology
- 0.6 mL of 2 wt% solutions used
- TA Instruments AR-G2 rheometer with a 40 mm 2° cone and plate geometry used with an angular frequency of 1 rad/s and 5% strain
- Heating/cooling rate = 2.5 °C/min from 5 to 80 °C

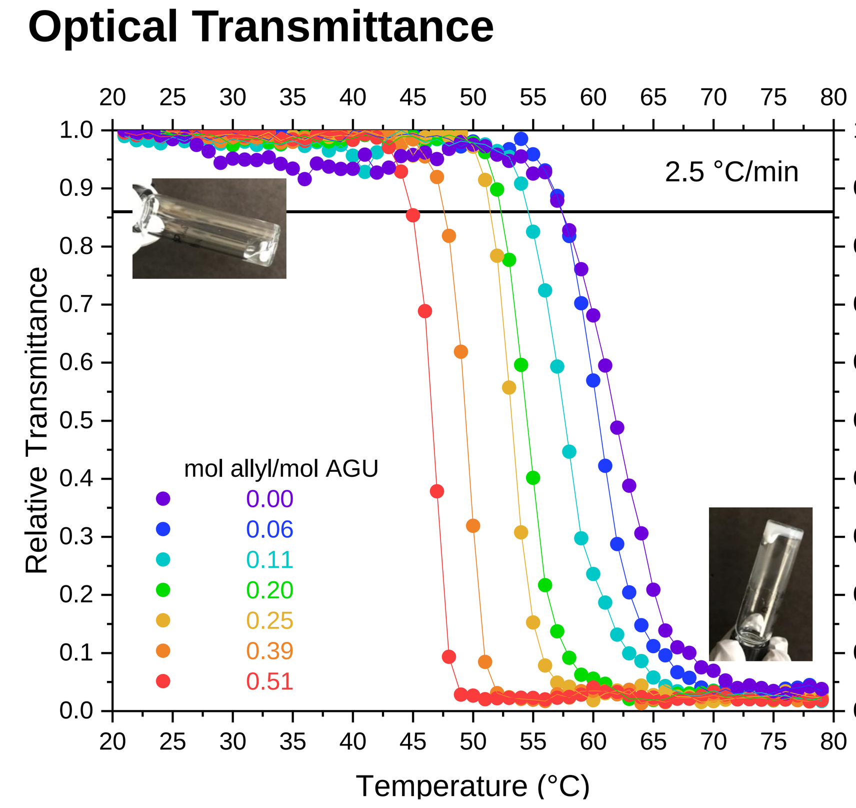
Results and Discussion

Reaction Scheme and Proton NMR Spectroscopy



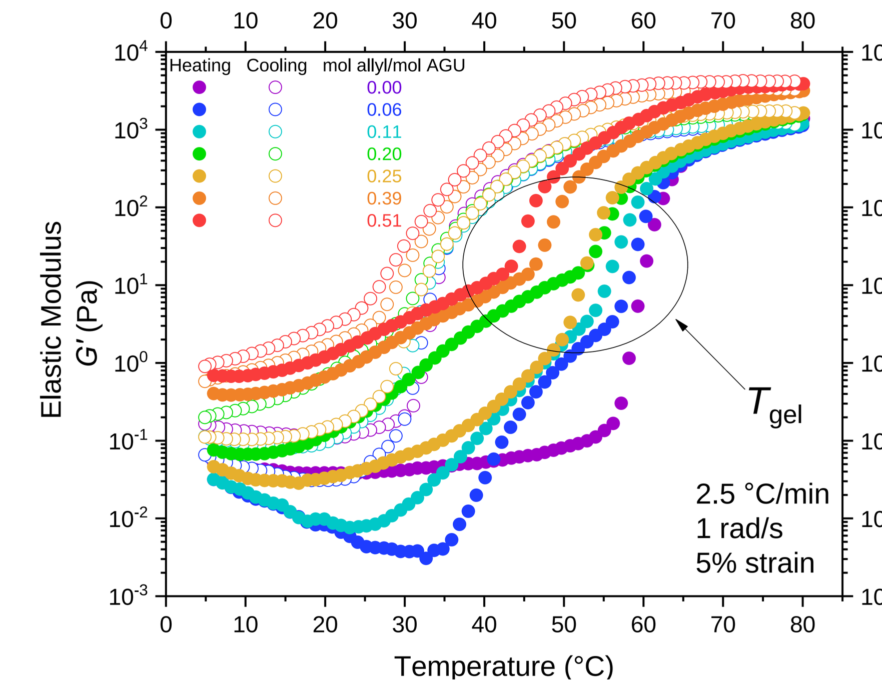
Mol allyl/mol AGU pertains to the number of allyl groups substituted per AGU, shown by peak **a**, in comparison to the single hydrogen shown by peak **c**.

Optical Transmittance



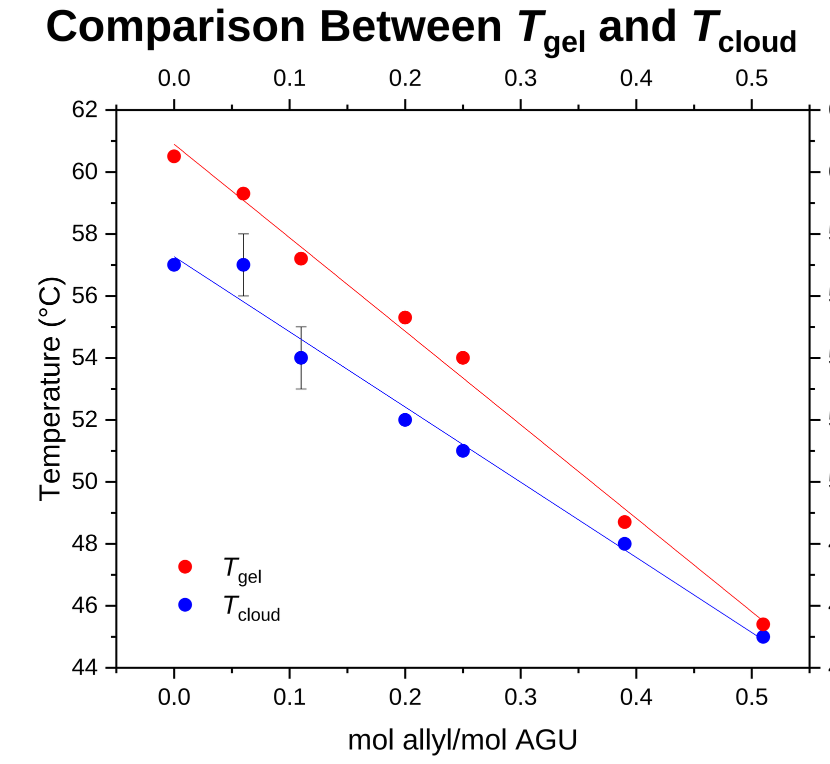
T_{cloud} decreases as number of allyl substituents increases

Rheology



T_{gel} decreases as number of allyl substituents increases

Comparison Between T_{gel} and T_{cloud}



- $T_{gel} \approx T_{cloud}$
- T_{gel} slightly higher due to the lower effective heating rate in the optical transmittance experiment as gelation in MC solutions is rate-dependent

Conclusion

- Gelation and phase separation occur concurrently in allylated MC solutions
- Increase in allylation causes early onset of phase separation, gelation, and fibril formation due to its increasing hydrophobicity
- Lower gel point expands application uses and temperatures

Future Work

- Repeat trials for rheological and optical transmittance measurements to construct a more accurate comparison diagram
- Characterization of the polymer solutions through static and dynamic light scattering, cryo-TEM, and small angle X-ray scattering
- Grafting with thiol-terminated compounds of varying molecular weights and stereochemistry to better understand the mechanism of fibril formation

Acknowledgements

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References

Arvidson, S. A. et al. *Macromolecules*. **2013**, *46*, 300-309.
Lott, J. R. et al. *Biomacromolecules*. **2013**, *14*, 2484-2488.