Comparing the rheological properties of dextran and dextran esters

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Introduction

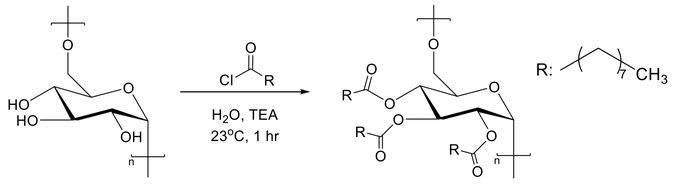
- **Long termgGoal:** Developing polysaccharide-based pressure sensitive adhesives (PSAs)
- PSAs are non-reactive adhesives that bond to a substrate by application of light pressure.
- Polysaccharides possess high glass transition temperatures (T_g) (PSAs require low T_g)
- Previous studies confirmed attaching side chains to polysaccharides alter the thermal properties[1]
- As PSAs are used in the vicinity of the rubbery state, understanding the behavior of polymeric chains is of importance → Polymer solution rheology

Research Question

- How does the attachment of substituents affect the rheology of polysaccharides?

Methods

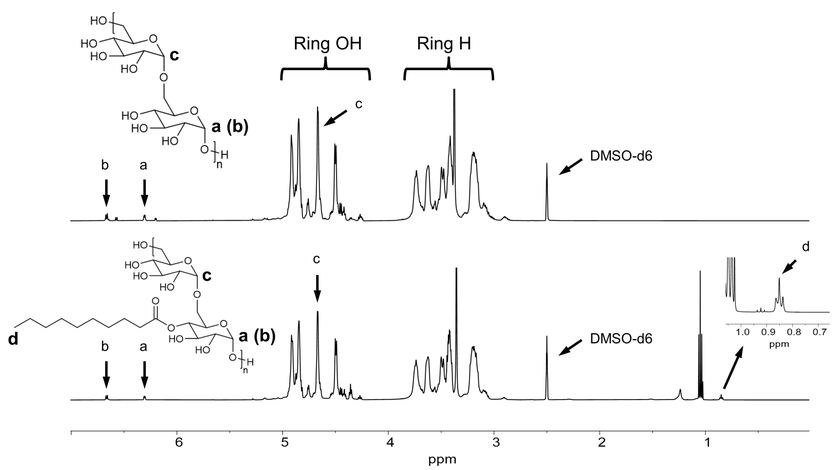
- **Dextran esterification**
  - Materials
    - Dextran 5 (M_w: 5,000 g/mol)
    - Decanoyl chloride
    - Triethylamine (TEA)



- **Structural characterization**
  - ^{1}H-NMR
- **Rheological properties**
  - Ubbelohde viscometer (size: 1C, inner diameter of capillary tube: 0.8 mm)
  - Measured at 25, 40, 60°C

Results

- **^{1}H-NMR spectra of dextran and decanoyl dextran**

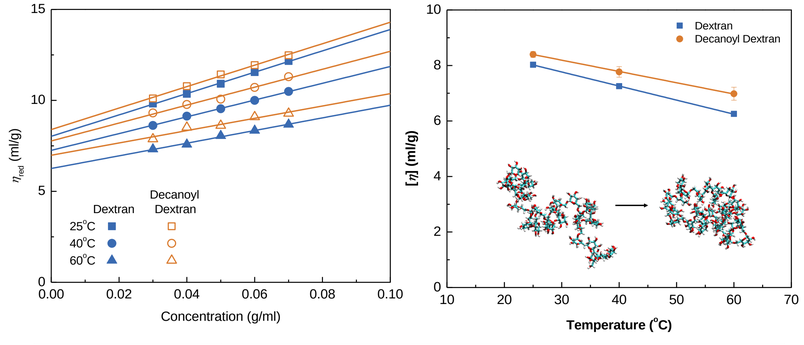


	α (%)	β (%)	M_n (g/mol)	DS (%)
Dextran	45	55	2,276	-
Decanoyl Dextran	46	54	2,895	0.4

- End group analysis: Ratio of α,β structures, number average molecular weight (M_n) (For low M_w dextrans)[2]
- Confirmation of substitution: New peak at ~8.5ppm
- Degree of substitution: Ratio of the integrated area of CH_3 protons from substituent to the area of anomeric protons (α(1,6) linkages) of dextran

- **Intrinsic viscosity ([η]) of dextran and decanoyl dextran**
  - [η] is a measure of M_w and hydrodynamic volume (Flow behavior of a single polymer chain)

$$[\eta] = \lim_{c \to 0} \eta_{red}$$



	[η] (ml/g)		
	25°C	**40°C**	**60°C**
Dextran	8.03	7.25	6.26
Decanoyl Dextran	8.40	7.77	6.98

- Both dextran and decanoyl dextran show decreasing [η] with increasing temperature, indicating contraction of coils
- Higher [η] found for decanoyl dextran, suggesting higher M_w and/or larger hydrodynamic volume

Conclusion

- Decanoyl dextran exhibited longer times when flowing down the capillary of the Ubbelohde viscometer than dextran, resulting in an increase of intrinsic viscosity

References

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2. Dupayage, L., Save, M., Dellacherie, E., Nouvel, C., & Six, J. L. (2008). PMMA-grafted dextran glycopolymers by atom transfer radical polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, *46*(23), 7606-7620.

* Computational images adapted from Parisa Farzeen (Dr. Deshmukh group)

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