2014 Taste of Research Summer Scholarship Program

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Smart Polymers:
The Thermo-responsivity of Graphene Oxide Hybrids

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Fundamental and Enabling Research

Objectives

- Synthesise polymer-graphene oxide (GO) nanogels that contract at different temperatures.
- Investigate polymer-GO hybrids that form stable emulsions and improve on their stability.
- Characterise the different hybrids and analyse the data obtained.

Background

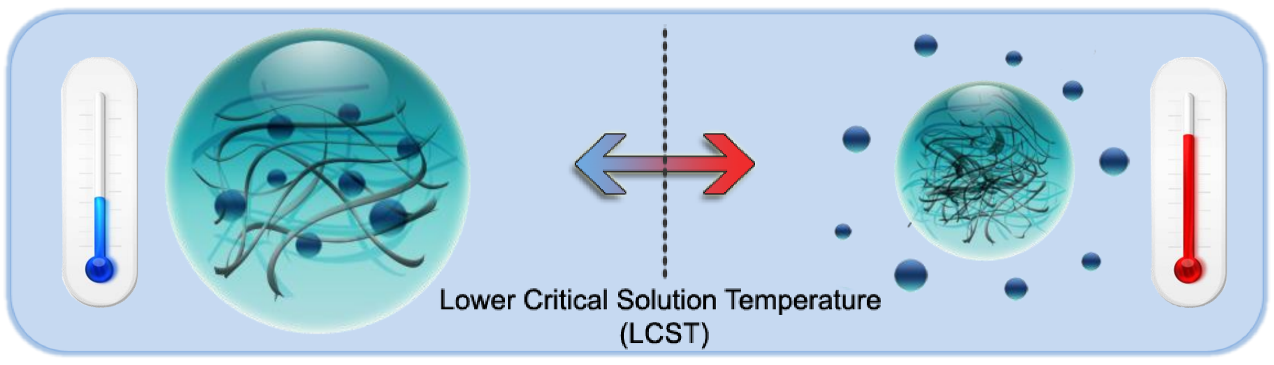


Figure 1: Poly(N-Isopropylacrylamide) (pNIPAM) chains contract and expel water molecules upon heating , in a reversible process

Certain "smart" polymers can shrink or swell when above or below a transition point known as the **Lower Critical Solution Temperature** (LCST):

- *Below the LCST, polymer chains are hydrophilic, bonding to water and swelling.*
- *Above the LCST, the polymer turns hydrophobic, expelling water and shrinking.*

One of these smart polymers is pNIPAM, used extensively in my research. Cross-linked pNIPAM nanogels can be prepared using N,N'-Methylenebisacrylamide (BIS) and Methacrylic Acid (MAA).

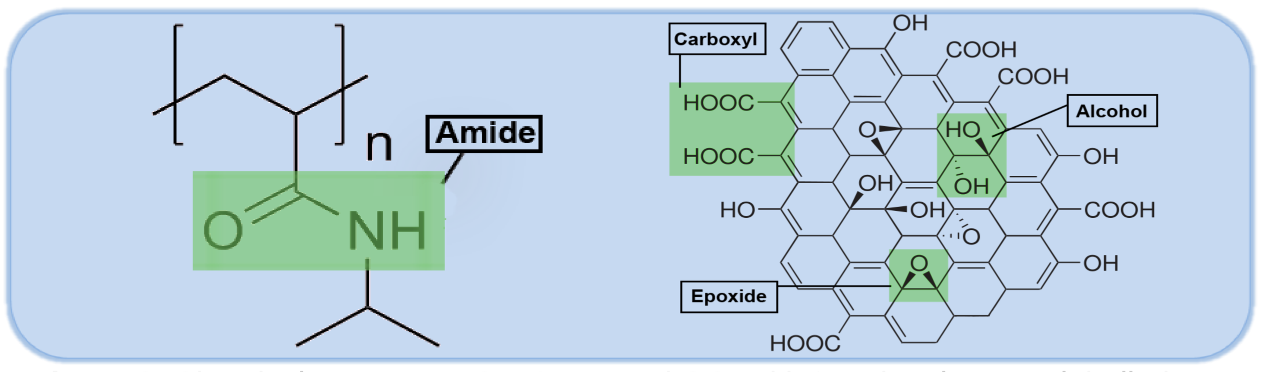


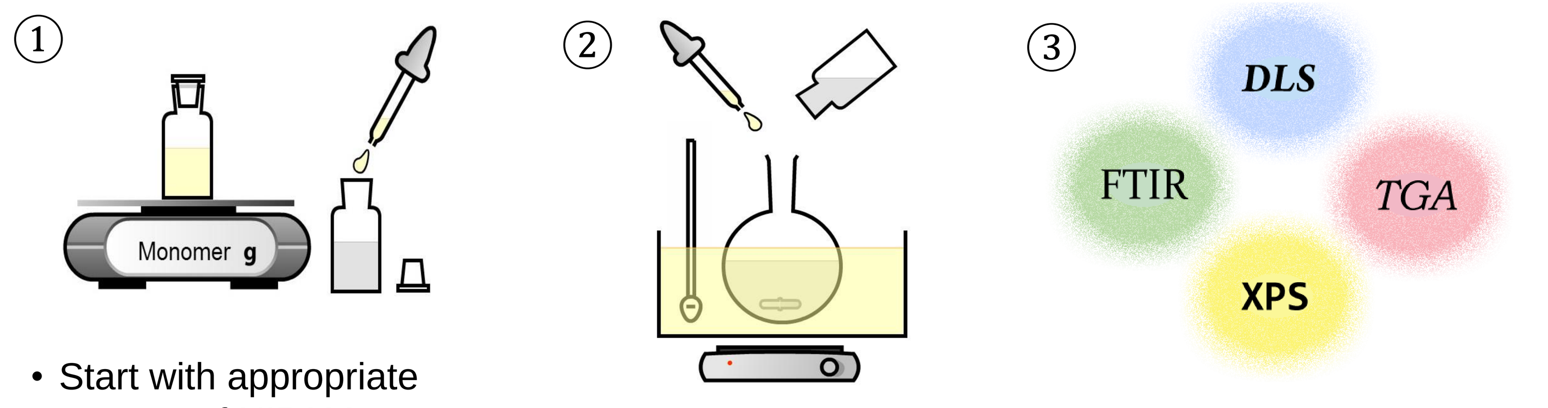
Figure 2: Chemical structures of pNIPAM and GO, with functional groups labelled

Graphene Oxide (GO) is the product of graphite oxidation. With the recent discovery of graphene and its exciting properties, GO is under scrutiny as a precursor to graphene integrated materials. The oxygen functionalities on GO result in its good dispersibility in solvents. My research is on GO's effect on the thermo-responsivity of smart polymers.

Methodology

Initially oxidise and purify Graphite to produce an initial bulk GO sample, then sonicate to exfoliate and dilute GO sheets.

Figure 3: The typical steps in emulsion synthesis



①
- Start with appropriate amount of NIPAM, cross-linker, and co-monomer dissolved in water.
- Vary GO concentration and deoxygenise with N_2 gas.

②
- Add initiator to solution in a round-bottom flask at 40°C.
- Ramp up temperature to 70°C for ~12 hrs.

③
- Characterise the nanogels.
- Mainly by: Dynamic Light Scattering over a temperature range to ascertain the LCST.

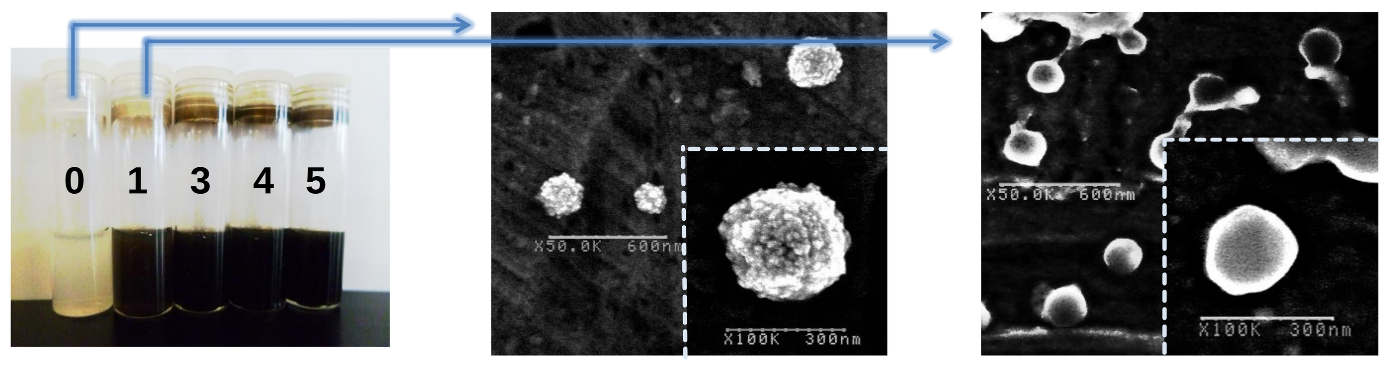


Figure 4: Sample tubes of pNIPAM with 0,1, 3,4, 5% w/w GO, with Scanning Electron Microscope comparisons of pNIPAM and pNIPAM 1%GO

Dynamic Light Scattering (DLS) Equipment

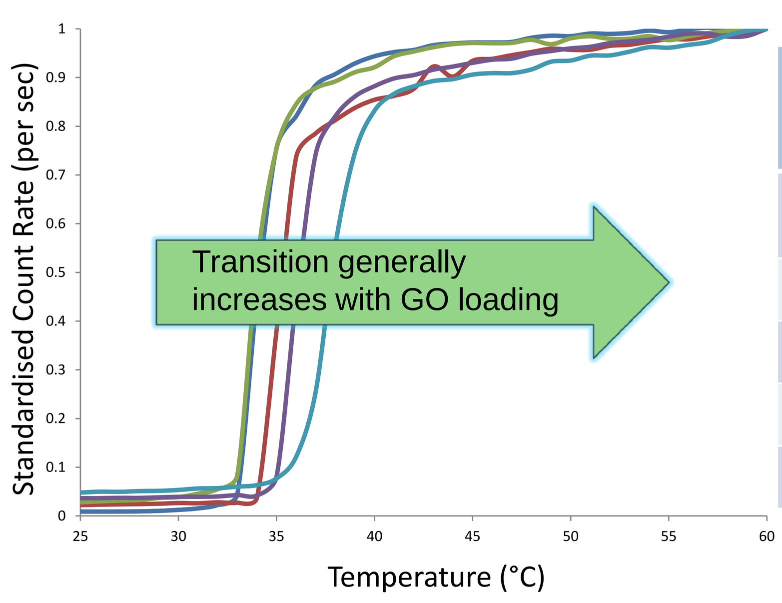
- *DLS uses the scattering of laser light by particles to measure their size in water.*
- *The scattered light intensity (Count Rate) is related to the size and degree of swelling at a certain temperature.*
- *As our particles shrink with temperature, they scatter significantly more light, which we can use to monitor their thermo-responsivity.*

Results/Discussion

Graphs of **Count Rate** against **Temperature** for various hybrid polymers:

Variation with %GO Loading

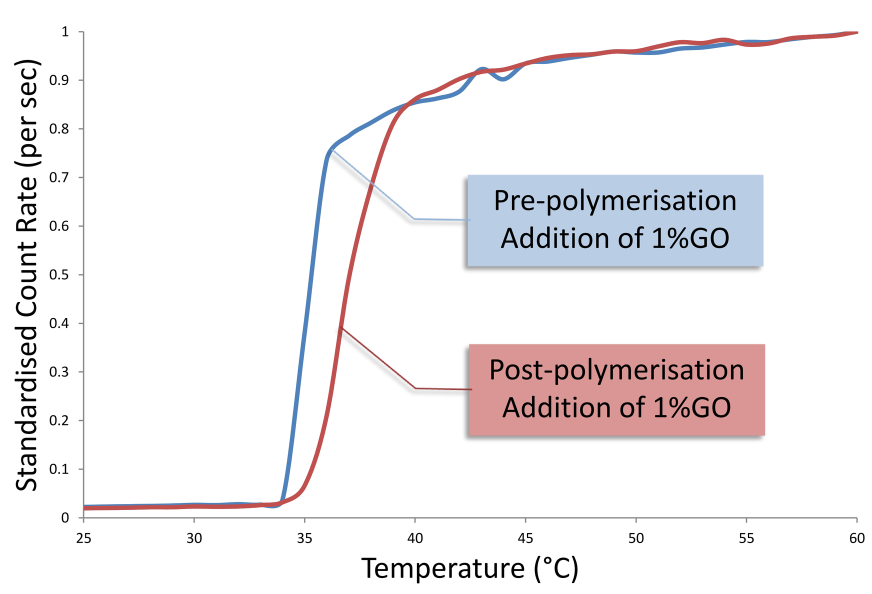
- General trend: The LCST increases with GO loading.
- Hydrogen bonding between pNIPAM and GO sheets gives us the ability to tune the LCST of the system.



GO Loading (wt. %)	Transition Temp. (°C)
0% (Control)	34.2
1%	35.3
3%	33.9
4%	36.2
5%	37.8

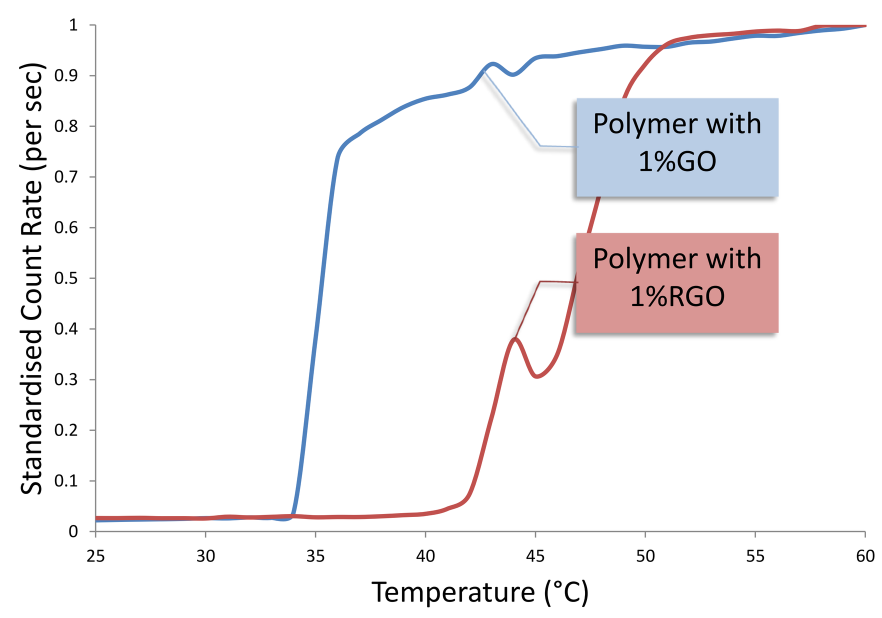
Variation with Order of Addition

- The order of adding GO was varied: GO was either added before polymerisation, allowing assimilation, or mixed in after.
- There was a significant difference in the LCST of pre/post-polymerisation addition hybrids.



Variation with Oxidation State

- GO was reduced with hydrazine monohydrate, producing Reduced Graphene Oxide (RGO).
- pNIPAM-RGO displayed the largest LCST increase.



Applications

Biomedicine:
- Thermo-responsive particles have seen use in medicine for the controlled release of drugs.
- Being able to control the LCST is important for this.
- GO is non-toxic: Polymer-GO hybrids are potentially viable materials.

Water Remediation:
- Using a similar approach as before, macroscopic pNIPAM-GO gels were prepared (Fig. 5).
- The thermo-responsive behaviour of these gels could be used to remove water pollutants.

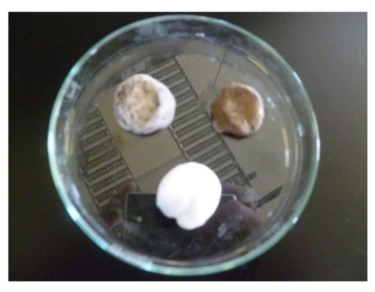


Figure 5: Macroscopic gels in the swollen state

Sensory Materials:
- pNIPAM nanogels are commonly used to make colloidal crystals for optical sensors.
- GO can be used to tune the LCST of these materials for various applications.

Conclusion

- pNIPAM-GO hybrid nanogels form stable emulsions upon polymerisation in water.
- Varying the GO loading enables the LCST of these nanogels to be varied.
- The order of GO addition and extent of GO oxidation strongly influence the thermal response of these systems.

References:

(1) Thickett, S. C.; Zetterlund P. B. *ACS Macro Lett.* **2013**, 2, 630

(2) Dong, J.; Weng, J.; Dai, L. *Carbon* **2013**, 52, 326

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