

An Indian-Australian research partnership

**Project Title:** **Molecular simulation of the structure and dynamics of associative polymer solutions**
**Project Number** **IMURA0671 (3)**
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**Research Academy Clusters:**
**Highlight which of the Academy's CLUSTERS this project will address?**
*(Please nominate JUST one. For more information, see [www.iitbmonash.org](http://www.iitbmonash.org))*

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|---|--|
| 1 | <b>Material Science/Engineering (including Nano, Metallurgy)</b>                 |
| 2 | <b>Energy, Green Chem, Chemistry, Catalysis, Reaction Eng</b>                    |
| 3 | <b>Math, CFD, Modelling, Manufacturing</b>                                       |
| 4 | <b>CSE, IT, Optimisation, Data, Sensors, Systems, Signal Processing, Control</b> |
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| 8 | <b>HSS</b>   |

**The research problem**

*Associative polymers* are intricate and partially structured systems that have recently attracted a great deal of interest. These polymers typically consist of two types of segments (or *blocks*): those that are hydrophilic (water-soluble) and those that are hydrophobic (water-insoluble). As a result of the dual character of these molecules, they serve, even at low concentration, as effective rheological modifiers – a property which is responsible for their use in various industrial applications in which careful control of the

rheology of the solution is required, e.g., paints, foods, and pharmaceuticals. Examples of these systems include “HEUR” polymers, which have hydrophobic *end groups* and “HASE” polymers, with hydrophobic groups *distributed* along the polymer backbone. When dissolved in water, the hydrophobic segments seek to minimize their exposure to water, leading to a force that drives the association between them, and gives rise to both intra- and intermolecular temporary domains or junctions. The network of polymeric strands that is formed is temporary since the junctions that hold the network together break and re-form continuously due to thermal fluctuations. Depending on the locations of the hydrophobic groups on the polymers, different *micellar* structures are formed on the molecular scale, with polymeric segments forming *loops*, *bridges*, or *dangling chains*. The complex rheological behaviour of associative polymers emerges from the dynamical swapping of these loops, bridges, and dangling chains in response to the deformation imposed on the network. The structure and dynamics of these chains depends on a number of parameters such as temperature, polymer concentration, molecular weight, size and strength of hydrophobic segments, and the strength of the imposed deformation. As a result, the relationship between structure and the rheological response of associative polymers is very complex. Indeed, these types of physically associated networks demonstrate mechanical properties not seen in chemically cross-linked systems, including shear thinning at high strain rates, self-healing properties, and stress relaxation at long times. This combination of responsive and mechanical properties makes physically associated networks ideally suited for a wide variety of applications in natural and synthetic materials. A fundamental understanding of the *non-equilibrium* response of the temporary network of self-organized gel-like structures that form on the molecular scale is necessary for the rational design of new functional materials, and that of already existing synthetic and biological systems (where such reversible associations are known to drive a large number of processes from the molecular to physiological levels).

*Suggested reading:*

1. Tripathi, A.; Tam, K. C. & McKinley, G. H., Rheology and dynamics of associative polymers in shear and extension: theory and experiments, *Macromolecules*, 39, 1981-1999, 2006.
2. Myung, J. S.; Winkler, R. G. & Gompper, G., Self-organization in suspensions of end-functionalized semiflexible polymers under shear flow, *J. Chem. Phys.*, 143, 243117, 2015.
3. Sing, M. K.; Wang, Z.-G.; McKinley, G. H. & Olsen, B. D., Celebrating Soft Matter's 10th Anniversary: Chain configuration and rate-dependent mechanical properties in transient networks, *Soft Matter*, 11, 2085-2096, 2015.

## **Project aims**

There have been many experimental studies of the viscoelastic properties of associative polymer solutions and a number of theoretical models based on transient network theory that appear to capture, qualitatively, experimental observations. Further, Monte Carlo and molecular dynamics simulation studies of coarse-grained models of end-functionalized polymers in solution have shown the formation (at thermal equilibrium) of self-organized scaffold-like network structures above a critical attraction strength and within a range of concentrations. Simulations also predict flower-like micellar aggregates for flexible polymers, while for stiffer polymers, liquid-crystalline-like order of adjacent polymers and inter-connected structures are observed. However, there are many rheological properties of associative polymer solutions whose molecular origins are yet

to be understood. These include, (i) shear thickening at moderate shear rates in steady shear flow followed by marked shear thinning at high shear rate, (ii) a decrease in the critical shear rate at which onset of shear thickening occurs as the association strength or concentration increases or temperature decreases, (iii) the existence of a dual relaxation behaviour, with a short time relaxation process attributable to the lifetime of hydrophobic junctions, and a long time process attributable to network relaxation, and (iv) the apparent exponential increase in extensional viscosity with an increase in hydrophobicity and concentration of the polymers. The extensional properties of associative polymer networks, in particular, remains virtually unexplored even though extensional rheology plays an important role in many commercial applications of associative polymers such as spray formation and paint applications.

The aim of this project is to investigate the non-equilibrium structural and dynamical properties of associative polymer solutions by mesoscale hydrodynamic simulations. Both the structural and rheological properties will be analyzed for various deformation rates in shear and extensional flow. In particular, the relationship of the breakup of the initial scaffold-like network structure at low deformation rates and the loss of structural integrity at high deformation rates, to observed macroscopic rheological properties will be studied. Further, the role of chain flexibility, temperature, molecular weight and concentration will be systematically examined.

A combination of a coarse-grained model of associating polymers and the mesoscale Brownian dynamics simulation technique will be used to carry out the study. Mesoscale hydrodynamic simulation approaches are essential, because only they allow one to reach the large length and time scales which are required to capture the long structural relaxation times in flow. In addition and most importantly, Brownian dynamics simulations naturally include thermal fluctuations, which are indispensable for a proper description of polymer solution dynamics.

### **Expected outcomes**

We want to elucidate the general principles of structure formation of associative polymer solutions under non-equilibrium conditions. Because the mechanical properties of such solutions are critical to their use in natural or engineered applications, a fundamental understanding of the physically associating network dynamics is critical to the design of these systems. The achieved insight will be useful to understand the behaviour of a broad spectrum of experimental systems, ranging from synthetic polymers, to biological macromolecules.

### **How will the project address the Goals of the above Themes?**

The research in this project addresses the Academy cluster “Math, CFD, Modelling, Manufacturing”. The major benefit is an understanding of the dynamics of associative polymer solutions. This is important on a fundamental scientific level and also because understanding the molecular processes involving structural changes is crucial for developing an adequate description of the origin of viscoelasticity in these solutions. This Project offers research training to a post-graduate student, exposing him/her to a broad range of advanced computer simulation techniques. The proposed research will build expertise in India and Australia in advanced simulation methods that are currently the domain of a select few research groups across the world.

## Capabilities and Degrees Required

The following capabilities are essential:

1. Excellent training in mathematics and numerical methods
2. Proven experience with computer programming in high level languages
3. Ability to write and communicate fluently
4. Strong background in Engineering/Physics
5. Candidates without this background will not be considered

## Potential Collaborators

This project will be carried out in collaboration with Professor Gareth McKinley of MIT, USA (<http://meche.mit.edu/people/faculty/GARETH@MIT.EDU>). McKinley's group have been carrying out rheological measurements of saliva as a non-invasive diagnostic for pathology and disease. In particular, on the shear and extensional rheology of saliva, and the temporal stability in the face of enzymatic degradation. Extensional rheometry data of saliva samples at various ages shows that the relaxation time of these highly elastic but low viscosity aqueous solutions decrease as a function of age. The viscoelastic properties of saliva can primarily be attributed to the presence of large glycoproteins in solution. It is well known that these glycoproteins physically associate and interact with each other and their surroundings via disulphide linkages, ion-mediated crosslinking and hydrogen bonding interactions to form a very weak hydrogel or 'pre-gel'. The aim of the research collaboration is to verify if the computer simulation algorithms developed in the project are able to accurately capture the behaviour of saliva using parameters that respect the known dimensions and properties of the network, and can systematically account for temporal changes in the rheology through a progressive decrease in the molecular weight of the network strands.

Select up to **(4)** keywords from the Academy's approved keyword list (**available at [www.iitbmonash.org](http://www.iitbmonash.org)**) relating to this project to make it easier for the students to apply.

Associative polymer dynamics, Gel network, Rheological properties, Molecular simulations