IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title:	**Sticky Polymers in Flow**	
Project Number	**IMURA1177**	
Monash Main Supervisor (Name, Email Id, Phone)	Prof. Ravi Jagadeeshan, ravi.jagadeeshan@monash.edu,	*Full name, Email*
Monash Co-supervisor(s) (Name, Email Id, Phone)		
Monash Head of Dept/Centre (Name,Email)	Prof. Sankar Bhattacharya, sankar.bhattacharya@monash.edu	*Full name, email*
Monash Department:	Chemical and Biological Engineering	
Monash ADGR (Name,Email)	Prof. Timothy Scott, timothy.scott@monash.edu	*Full name, email*
IITB Main Supervisor (Name, Email Id, Phone)	Prof. P. Sunthar, sunthar@che.iitb.ac.in,	*Full name, Email*
IITB Co-supervisor(s) (Name, Email Id, Phone)		*Full name, Email*
IITB Head of Dept (Name, Email, Phone)	Prof. Mahesh S Tirumkudulu, mahesh@che.iitb.ac.in,	*Full name, email*
IITB Department:	Chemical Engineering	

Research Clusters:

Highlight which of the Academy's CLUSTERS this project will address?
*(Please nominate JUST **one.** For more information, see www.iitbmonash.org)*

1	*Material Science/Engineering (including Nano, Metallurgy)*
2	*Energy, Green Chem, Chemistry, Catalysis, Reaction Eng*
3	*Math, CFD, Modelling, Manufacturing*
4	*CSE, IT, Optimisation, Data, Sensors, Systems, Signal Processing, Control*
5	*Earth Sciences and Civil Engineering (Geo, Water, Climate)*
6	*Bio, Stem Cells, Bio Chem, Pharma, Food*
7	*Semi-Conductors, Optics, Photonics, Networks, Telecomm, Power Eng*
8	*HSS, Design, Management*

Research Themes:

Highlight which of the Academy's Theme(s) this project will address?
(Feel free to nominate more than one. For more information, see www.iitbmonash.org)

1	*Artificial Intelligence and Advanced Computational Modelling*
2	*Circular Economy*
3	*Clean Energy*
4	*Health Sciences*
5	*Smart Materials*
6	*Sustainable Societies*
7	*Infrastructure*

The research problem

Several disparate phenomena, such as: (i) the flow behaviour of paints, coatings and inks [1] (ii) the treatment of diseases in the posterior segment of the eye [2] (iii) the development of food thickeners for people suffering from mastication and swallowing disorders [3] (iv) the designing of scaffolds with optimal characteristics for successful tissue engineering [4] and (v) the response of hagfish when attacked by predators [5], have all got one feature in common – they are based on the unique properties of supramolecular networks formed by associative (sticky) polymer solutions. Associative polymers are macromolecules with attractive groups [6], and the reason for their use in such a wide variety of applications is because the interactions between the attractive groups can be "tuned" by varying their number, strength and location on the polymer. This provides a means of exquisitely controlling the physical properties of associative polymer solutions. For instance, they are widely used as rheology modifiers in the coating, paint, water-treatment and enhanced oil-recovery industries, since their viscosity can be controlled by changing the temperature or concentration [1,7]. At sufficiently high concentrations, when the suspending medium is water, associative polymers form a transient viscoelastic network known as hydrogels. Hydrogels have found numerous applications as tissue engineering scaffolds, drug delivery carriers, soft electronics, and sensors [8]. In each of these applications, control over the microstructure and rheology is critical to obtaining the desired behaviour. A fundamental understanding of physically associating polymer dynamics is consequently essential for the rational design of these systems.

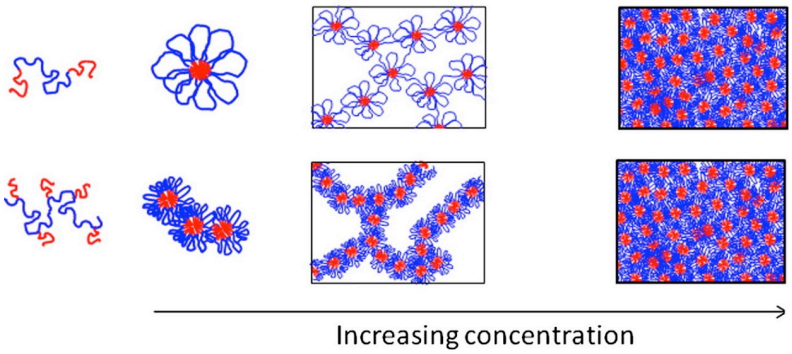

Fig. 1 Theorized aggregation of associative polymers. Reproduced from [12]. (Top) Telechelic polymers form bridges between associated clusters with increasing concentration. (Bottom) Multi-sticker chains form highly interconnected clusters in a broad range of concentration.

The associations between attractive groups that lead to the formation of reversible physical bonds can arise from several different interactions such as hydrophobic, ionic, metal coordination or hydrogen bonding [9]. Telechelic polymers have attractive groups at the chain ends, while multi-sticker polymers have attractive groups distributed along the polymer backbone. The structures formed in associative polymer solutions depend on the location and number of attractive groups per chain, the strength of the physical bonds, and on polymer concentration [10-12], as shown schematically for the two types of polymers in Fig. 1. The rheological behaviour of associative polymers emerges from the dynamical swapping between various chain conformations in response to the deformation imposed on the network. As a result, the relationship between structure and the rheological response of associative polymers is very complex.

In order to motivate the research proposed in this project, two different examples of published rheological data are discussed in turn. The differences in response between telechelic and multi-sticker polymers highlight the influence that molecular topology and dynamics have on

macroscopic observables. In each case, a predictive understanding of the macroscopic phenomena does not currently exist, and the goal of the present work is to bridge this gap.

Storage and Loss Moduli (Linear Rheology)

The loss and storage moduli characterize the elastic and viscous responses of a material as a function of shear frequency (inverse time scale). The intersection of these moduli as in Fig. 2(a) indicate a particular time scale on which a material relaxes. Systems of telechelic polymers are typically well described by a Maxwell model with a single relaxation time, as shown in Fig. 2(a) for a HEUR (hydrophobic ethoxylated urethane) solution [13]. On the other hand, multi-sticker systems typically exhibit broad power law relaxation spectrum [14-16] with no readily discernible characteristic time scale, as displayed in Fig. 2(b) for saliva [16]. The origin of the difference in behaviour between these two systems is currently not well understood theoretically.

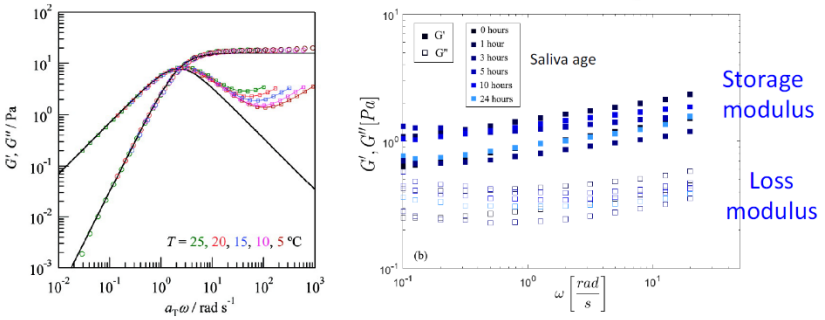

Fig. 2 Storage and loss moduli for (a) telechelic (reproduced from [13]), and (b) multi-sticker (reproduced from [16]) associative polymer systems.

Shear Thickening (Nonlinear Rheology)

Telechelic polymer solutions exhibit characteristic shear thickening behaviour at intermediate shear rates [13], as shown in Fig. 3(a), while this is not necessarily present in multi-sticker solutions [14]. Fig. 3(b) demonstrates the elimination of shear thickening with the addition of urea to a multi-sticker polysaccharide solution (Mamaku gum), due to the disruption of hydrogen bonds that are responsible for the development of the transient network [17]. The existence of shear thickening at intermediate shear rates is attributed to the delicate interplay of the finite extensibility of chain segments, and enhanced numbers of stress-bearing polymer strands resulting from the imposed shear flow [7]. Recent experimental observations [13], however, suggest that the network structure remains close to the equilibrium state and demands an alternative explanation for the presence of shear thickening. This highlights the need for Brownian dynamics (BD) simulations with molecular scale insight to resolve the issue [18]. Clearly, there is no general agreement regarding the origin of shear thickening in telechelic polymer solutions, nor is its absence in multi-sticker solutions clearly understood.

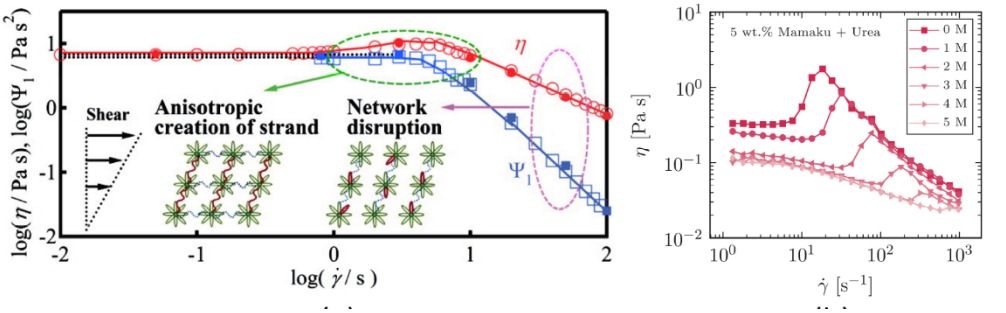

Fig. 3 Viscosity η as a function of shear rate $\dot{\gamma}$ in (a) a telechelic HEUR solution (from [13]), and (b) a Mamaku gum solution, with associative interactions mediated by the introduction of Urea (from [17]).

Project aims

The aim of this project is to lay the foundations for a theoretical approach to determine how microscopic topology and the strength/number of intermolecular interactions control the flow behaviour of model associative polymer solutions.

The systems studied under this proposal involve a broad range of time and length scales. For instance, routinely simulating every atom in polymer chain is infeasible. This is only made worse by considering solutions of chains and the surrounding solvent molecules. Some degree of coarse graining is necessary. One can't coarse grain all the way to continuum mechanics because at present there are no constitutive equations to map arbitrary microscopic components to macroscopic behaviour. The wide variety (see Fig. 4) of molecular architectures and chemical interactions available to engineers makes the construction of such a map a dauting task.

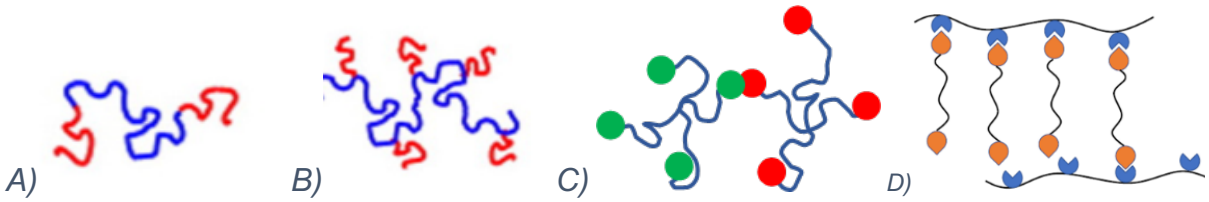

Fig. 4 An assortment of practically available polymers. A) Telechelic polymers have functional groups only at the ends. B) multi-sticker chains have active groups periodically. C) star polymers have multiple branches. D) Multi-component systems create structured networks.

Brownian Dynamics simulations can achieve this by coarse graining enough atomic details to make simulations tractable, while retaining the variety of competing interactions at the scale of k_B T. Segments of a polymer chain are modelled as points ("beads") which feel independent, fluctuating forces to produce Brownian motion. Beads are connected by springs to model the entropic tendency of a fluctuating chain to contract from its maximum extension. A chain can't pass through itself, so the beads are given a close-range repulsive interaction to create an excluded volume around a bead. Globs of chain drag on the solvent, causing long-range hydrodynamic interactions between beads.

All these features are found in modern Brownian Dynamics (BD) simulations. However, there is presently no simulation toolkit which supports the variety of molecular architectures and interactions available to engineers. This project will develop a novel multi-particle mesoscopic simulation algorithm for describing the dynamics of associating polymers with the flexibility to model even systems with a mixture molecular architectures and associative interactions. Simulation predictions will be compared with the results of experimental data in the literature.

References

1. Glass, J. E.; Schulz, D. N. & Zukoski, C. F., in Polymers as Rheology Modifiers, vol. 462, ACS Symposium Series 2–17, 1991.
2. Kirchhof, S.; Goepferich, A. M. & Brandl, F. P., Euro. J. Pharmaceutics and Biopharmaceutics, 95, 227–238, 2015.
3. O'Leary, M.; Hanson, B. & Smith, C., J. Food Sci., 75, E330–E338, 2010.
4. El-Sherbiny, I. M. & Yacoub, M. H., Global Cardiology Science and Practice, 2013, 38, 2013.
5. Böni, L.; Fischer, P.; Böcker, L.; Kuster, S. & Rühs, P. A., Sci. Rep., 6, 30371, 2016.

6. Winnik, M. A. & Yekta, A., Current Opinion in Colloid & Interface Science, 2, 424–436, 1997; Rubinstein, M. & Dobrynin, A. V., TRIP, 5, 181–186, 1997; R. G. Larson, The structure and rheology of complex fluids. New York: Oxford University Press, 1999.
7. Tripathi, A.; Tam, K. C. & McKinley, G. H., Macromolecules, 39, 1981-1999, 2006.
8. Seiffert, S., Ed., Supramolecular Polymer Networks and Gels, vol. 268. Springer International Publishing, 2015; Voorhaar, L. & Hoogenboom, R., Chem. Soc. Rev., 45, 4013–4031, 2016; Tsitsilianis, C., Soft Matter, 6, 2372–2388, 2010.
9. Tanaka, F., Polymer Physics. Cambridge University Press, 2011.
10. Pellens, L.; Ahn, K. H.; Lee, S. J. & Mewis, J., J Non-Newton Fluid, 121, 87-100, 2004.
11. Regalado, E. J.; Selb, J. & Candau, F., Macromolecules, 32, 8580–8588, 1999.
12. Chassenieux, C.; Nicolai, T. & Benyahia, L., Current Opinion in Colloid & Interface Science, 16, 18–26, 2011.
13. Suzuki, S.; Uneyama, T.; Inoue, T. & Watanabe, H., Macromolecules, 45, 888–898, 2012.
14. Mewis, J.; Kaffashi, B.; Vermant, J. & Butera, R. J., Macromolecules, 34, 1376–1383, 2001.
15. Holten-Andersen, N.; Jaishankar, A.; Harrington, M. J.; Fullenkamp, D. E.; DiMarco, G.; He, L.; McKinley, G. H.; Messersmith, P. B. & Lee, K. Y. C., J. Mater. Chem. B, 2, 2467–2472, 2014.
16. Wagner, C. & McKinley, G. H. J. Rheol., 61, 1309-1326, 2017.
17. Jaishankar, A.; Wee, M.; Matia-Merino, L.; Goh, K. K. T. & McKinley, G. H., Carbohydrate Polymers, 123, 136–145, 2015.
18. Ianniruberto, G. & Marrucci, G., Macromolecules, 48, 5439–5449, 2015.

What is expected of the student when at IITB and when at Monash?

Expected work at IITB

At IITB, the student would complete his/her course work and will start working on the project. The course work will be designed to obtain a working knowledge of Statistical Mechanics, Polymer Physics, Molecular Dynamics and the appropriate background in Mathematics. This will make the student ready for the next stage where he/she actually starts working on the specific project. Early work will involve understanding the different currently existing models for polymer solutions based on Polymer Kinetic Theory. At an early stage in the PhD, the student will visit Monash to carry out simulations, which would be continued in IITB after he/she comes back from Monash.

Contributions and supervision responsibilities of IITB supervisor

IITB supervisor will take care of the student's course work at IITB. With the mutual consent of the supervisor at Monash, he/she will chalk out the courses to be taken by the student. In addition, it is the IITB supervisor's responsibility to connect the student with the research problem and start training the student with simple representative problems. The long-term task would be to supervise and guide the student towards the completion of his/her project after he/she comes back from Monash.

Expected work at Monash

In stage 1, the student will focus on developing new mesoscopic simulation methods to predict the dynamics of these model associating polymers. Initially, simulations will be carried out to characterise the equilibrium and close to equilibrium micellar and network structures on the molecular scale and ensure that rheological and scattering observations are accurately captured by the coarse-grained models used in the simulations. Subsequently, the predictions of the simulation models for shear and extensional flow will be compared with experimental observations for these flows. An iterative process will be adopted whereby the model will be

fine-tuned until satisfactory agreement between predictions and experiments is achieved. In stage 2, the validated simulation methods will be used to generate the rheological properties of associating polymer solutions with more complex molecular architecture and predictions will be compared with experiments on systems with the same topology in order to validate simulation predictions.

Based on the progress achieved, the student will continue to work on the project after returning to IITB.

Contributions and supervision responsibilities of Monash supervisor

The protocol for the development of Brownian dynamics simulations algorithms is well established in Jagadeeshan's group, and consequently, the analytical and numerical tools for tackling the proposed problems are readily available. His role is to provide the technical expertise, to guide the student, to coordinate the various activities of the project, to manage the budget, and to ensure that the aims and objectives of the project are met.

Expected outcomes

1) This project will lead to an unprecedented understanding of the role of position, density and lifetime of stickers on equilibrium dynamics, and unravel the relative importance of the various time scales involved in the relaxation of polymers in the network.
2) Examining the change in the dynamic moduli from being simple Maxwell like to being essentially featureless, as the sticker location and density is changed from being telechelic to multi-sticker, will lead to significantly new insight into the origin of scale free power law relaxation behaviour.
3) Unambiguously deciphering the origin of the shear thickening mechanism in shear flows of associating polymer solutions will resolve the conflicting mechanisms currently proposed in the literature. The proposed simulations will for the first time systematically elucidate the relative roles played by the rate of reversible bond association/dissociation, and network connectivity, on the extent of strain hardening and the concomitant occurrence of either brittle fracture or filament thinning in extensional flows.
4) The successful comparison of experiments and simulations on systems with complex molecular topology will constitute a big step towards the design of macromolecular architectures with controlled molecular interactions between attractive groups in order to obtain predictable rheological behaviour.

These outcomes will result in high quality journal publications within the fields of polymer dynamics and soft matter, with exemplar outputs demonstrated in recent publications from the participating academics.

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

The mechanical properties of associative polymer networks are critical to their use in natural or engineered applications, and a fundamental understanding of the physically associating network dynamics is critical to the design of these systems. The insights from the proposed

research will be useful to understand the behaviour of a broad spectrum of experimental systems, ranging from synthetic self-associating polymer systems to biological macromolecules, and will enhance Australia's ability to design and produce application-specific associative polymers. The potential applications of such supramolecular networks are very broad; ranging from biocompatible drug-eluting hydrogels with rheological properties designed to flow under strong deformations but then spontaneously develop elasticity and 'gel' in place, through custom design of liquid foodstuffs with controllable properties for treatment of diseases such as oral dysphagia (swallowing disorder) to advanced engineering design of complex fluids and gels (e.g. for transport of rock cuttings, mud control and enhanced oil recovery) in the oil gas & minerals sectors.

The chemicals and plastics manufacturing industry is the second largest manufacturing sector in Australia, and is consequently a significant contributor to Australia's economy, employing more than 60,000 people. The sector also supports many other industries like the food, automotive, construction, packaging, medical, agriculture, and mineral processing industries. Research that enables the sector to be dynamic, globally competitive and highly valued is of vital importance to Australia's economy. There is currently a vibrant and active research community in Australia using applied polymer chemistry to engineer innovative polymeric materials with controllable rheology for use in the mining/petrochemical sectors. There is also considerable activity in the development of nano-particle-doped and injectable hydrogel systems and tissue scaffolds for biomedical applications. However, research directed towards fundamental quantitative understanding of the specific microstructural features and interaction energies that ultimately control the ensuing thermomechanical properties is currently not being pursued in Australia, and the proposed research is expected to provide the needed expertise and molecular insight to enable rational a priori selection and design of supramolecular systems with optimal material properties.

Potential RPCs from IITB and Monash

Dr Prabhakar Ranganathan (Monash) - expert in soft matter and computer simulations.
Dr Rico Tabor (Monash) – expert in Soft Matter
Dr Rajarshi Chakrabarti (IITB) - expert in polymer physics.
Dr Ranjith Padinhateeri (IITB) - expert in polymer physics.

Capabilities and Degrees Required

The candidate should satisfy at least five of the following criteria:

1) Bachelor's degree in Engineering, Math, or Physics
2) At least one credited course in Differential Equations
3) At least one credited course in Numerical Methods
4) At least one credited course in Computer Programming
5) At least one mini-project with computer programming in high level languages
6) Should have appeared for JEE (Mains)

Students that do not meet these requirements will not be considered.

Necessary Courses

The student will need to do courses in advanced mathematical methods, statistical mechanics, soft matter and computational methods. There are several courses offered at IITB that meet these requirements. For instance, the following are examples of courses that IITB-Monash Academy students of Jagadeeshan have completed previously:

CH 814 Fundamentals of Molecular Energetics and Dynamics
CH 576 Statistical Mechanics
CL 613 Special Topics in Complex Fluids
CL 602 Mathematical and Statistical Methods in Chemical Engineering
CL 651 Rheology of Complex Fluids
PH 550 Soft Matter Physics
CL 701 Computational Methods in Chemical Engineering
PH 543 Advanced Statistical Mechanics

The student will be advised to take similar courses in order to pick up the required background.

Potential Collaborators

This project will be carried out in close collaboration with Professor Gareth McKinley of MIT, USA (https://meche.mit.edu/people/faculty/GARETH@MIT.EDU). Professor McKinley has an ongoing interest in sticky polymer solutions, and experiments carried out by his group will be used to validate the analytical and simulation approaches developed in the current project.

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

Computer Simulation, Modelling and Simulation, Computational and Theoretical Chemistry