IITB-Monash Research Academy

An Indian-Australian research partnership

Indian Institute of Technology Bombay | MONASH University

Project Title:	**Simulating megasupramolecules for mist control and drag reduction**	
Project Number	**IMURA0802**	
Monash Main Supervisor (Name, Email Id, Phone)	Ravi Jagadeeshan, ravi.jagadeeshan@monash.edu,	*Full name, Email*
Monash Co-supervisor(s) (Name, Email Id, Phone)		
Monash Head of Dept/Centre (Name,Email)	Mark M. Banaszak Holl, mark.banaszakholl@monash.edu	*Full name, email*
Monash Department:	Chemical Engineering	
Monash ADGR (Name,Email)	Emanuele Viterbo, Emanuele.Viterbo@monash.edu	*Full name, email*
IITB Main Supervisor (Name, Email Id, Phone)	P. Sunthar, sunthar@che.iitb.ac.in,	*Full name, Email*
IITB Co-supervisor(s) (Name, Email Id, Phone)	N/A	*Full name, Email*
IITB Head of Dept (Name, Email, Phone)	Ravindra D Gudi, ravigudi@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	*Advanced computational engineering, simulation and manufacture*
2	*Infrastructure Engineering*
3	*Clean Energy*
4	*Water*
5	*Nanotechnology*
6	*Biotechnology and Stem Cell Research*
7	*Humanities and social sciences*
8	Design

The research problem

The addition of small amounts of high–molecular weight polymers to flowing liquids can have profound effects on a variety of phenomena that seem out of proportion with the small concentration of polymers added to solution. It has been shown that dissolving parts-per-million quantities of long-chain flexible polymers into solution can lead to as much as 80% reduction in turbulent drag compared with that of the solvent alone. This significant reduction in friction has practical applications in reducing pumping cost for oil pipelines, and in the design of marine craft to achieve increased speed with less energy cost. Low concentrations of very high molar mass polymers have also been extremely successful in mist suppression of low viscosity fluids due to their effect on the breakup of liquid jets and drops. Mist is much more flammable than liquid fuel, and so the antimisting of aviation fuel by adding long polymers, interferes with mist formation and leads to improved fire-safe fuel. However, long polymer chains degrade during normal fuel handling and clog pumping equipment. Passage through equipment such as pumps snaps polymer chains through hydrodynamic tension (which builds up along the chain back-bone to a level that breaks covalent bonds), and it becomes inadequate for mist suppression. The challenge is to find a mist-control polymer that is stable during routine handling. Polymers with end-associative groups that can self-assemble and create supramolecules are a potential solution, since they can potentially break and reassociate reversibly, thus solving the problem of shear degradation. However, formation of megasupramolecules that self-assemble at low concentration has been difficult to realize since end-to-end association at low concentration predominantly leads to rings of a small number of chains, and flower-like micelles (see Fig. 1). Professor Julia Kornfield's group at Caltech has shown recently [1] that long telechelic (end-associating) polymers can self-assemble at low concentrations into solutions of megasupramolecules that have the extraordinary ability to control misting and to reduce drag. Using a lattice model, they first established that telechelic polymers with associating end-groups form linear and cyclic megasupramolecules if the polymer building blocks are long enough and the ends sticky enough, and that in particular, there is a narrow range of chain lengths in which the linear population dominates the ring population. The theoretical arguments inspired their attempts to develop an experimental system that would result in the formation of megasupramolecules. The key attributes of such molecules are their high extension in elongational flow, their ability to disassociate when subjected to strong shearing flow, and to reassociate under quiescent conditions. This essentially solves the problem of shear degradation that occurs due to chain scission in ultralong polymers, and renders such polymers unusable for the purposes of mist control. While this is undoubtedly an amazing demonstration of combining polymer physics and chemistry for the development of an industrially important application, there are still many aspects that need to be better understood. For instance, how does the variation of chain length, concentration and end-group stickiness, control (i) the relative populations of rings and linear chains at equilibrium (ii) the viscosity of the resulting megasupramolecular solutions in shear flows, and (iii) the magnitude of chain extension in elongational flows? Addressing these issues would make it easier to design the appropriate backbone polymers that would lead to specifically desired properties in the megasupramolecules. These questions can be answered by some recent advances in simulation methodology introduced by our group.

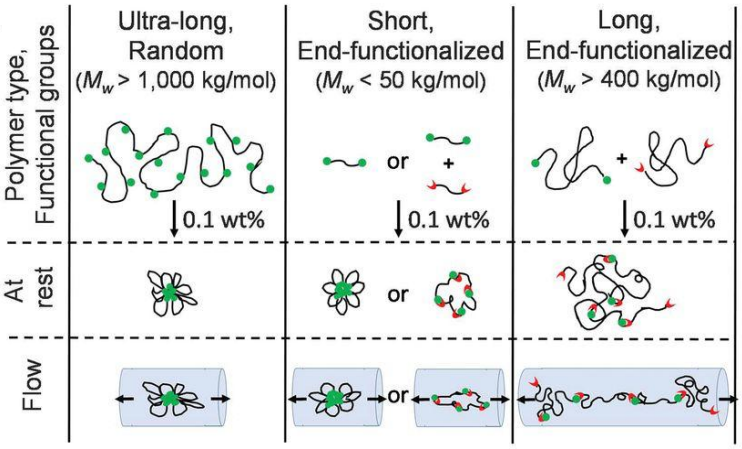

Fig. 1. Assembly of long *end-associating* polymers into megasupramolecules, compared with the assembly of long *randomly* functionalized associative polymers and *short* end-associative polymers into rings and flower-like micelles. Schematic polymer conformations at rest and in elongational flow are also shown. Reproduced from [1].

Project aims

There are two significant challenges to simulating the flow of end-associating polymer solutions. First, solution samples are typically prepared in a regime of concentration which necessitates modelling multi-body hydrodynamic interactions between polymer chain segment pairs. Importantly, this consideration

converts the simulation to a many-body one, which is computationally complex. The second challenge arises due to the presence of flow. The simulation boxes need to deform with the flow with high fidelity to maintain periodicity and allow simulations to proceed for sufficiently long times. Our group has recently overcome both of these challenges in the context of Brownian dynamics (BD) simulations, and successfully predicted both static and dynamic equilibrium properties, and non-equilibrium flow properties of semidilute solutions of *linear* polymers [2, 3]. This is a significant improvement on earlier models that are based on the behaviour of isolated chains in solution, since many-body interactions between multiple chains can now be taken into account. A mesoscopic BD simulation algorithm capable of computing end-associating polymer solutions will be developed in this project, which would be perfect for understanding the polymeric systems studied in Professor Julia Kornfield's group. There is an opportunity to combine experiments (in Julia Kornfield's lab) with simulations carried out in our group that would lead to a significant and predictive understanding of the behaviour of long telechelic polymers that end-associative to form megasupramolecules.

References:

[1] Ming-Hsin Wei, Boyu Li, David, R. L. Ameri, Simon C. Jones, Virendra Sarohia, Joel A. Schmitigal, and Julia A. Kornfield, "Megasupramolecules for safer, cleaner fuel by end association of long telechelic polymers". *Science*, 350 (6256). pp. 72-75 (2015).
[2] A. Jain, C. Sasmal, R. Hartkamp, B.D. Todd, J. R. Prakash, Chem. Eng. Sci., 121, 245–257 (2015).
[3] C. Sasmal, K. Hsiao, C. M. Schroeder, J. R. Prakash, J. Rheol., 61, 169–186 (2017).

Expected outcomes

The outcomes of the project will include:

1) A hydrodynamic coarse grained molecular model of end-associative polymers that captures the experimentally observed macroscopic behaviour.
2) Elucidation of the general principles relating the segment level structure of end-associative polymers to the macroscopic properties of the solution.

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 end-associative polymers, and their use in important practical applications such as drag reduction and mist control. This is important both on fundamental scientific and on practical levels because understanding the molecular processes involved in polymer association is crucial for developing an adequate description of the behaviour of such polymers. This Project offers research training to a post-graduate student, exposing them 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 (Either MSc in Physics or BTech/BE in Mechanical/Chemical Engg)

Potential Collaborators

This project will be carried out in collaboration with Professor Julie Kornfield of Caltech, USA (http://kornfield.caltech.edu/jak, http://kornfield.caltech.edu/research/Fuel)

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.

Modelling and Simulation, Computational Fluid Dynamics and Mechanics, Novel Functional Materials