





# **Bio-inspired Functional Adhesive Polymers**

Jonathan Millican, Lian Hutchings, Tim Ryan

Durham University, Durham, UK and Epigem Ltd., Redcar, UK, j.m.millican@durham.ac.uk

#### **1. Introduction**

Mussels are remarkable for their ability to stick to virtually any surface in a wet and hostile environment. Mussel Foot Proteins (MFPs) contain DOPA residues which provide the adhesion through the catechol on the side chain.

# 4. RAFT polymerisation of ADMA with other functional comonomers

- Homopolymers of ADMA have been synthesised by reversible additionfragmentation chain-transfer (RAFT) polymerisation.
- Dopamine is a naturally occurring neurotransmitter which can be polymerised from its natural or modified forms to mimic the adhesion of DOPA. (1)
- This work has focused on the synthesis, protection and polymerisation of dopamine methacrylamide for the design of functional surface coatings.



#### 2. Dopamine Methacrylamide (DMA)

- Dopamine and methacrylic anhydride were used to synthesise DMA; a monomer capable of forming functional adhesive polymers.
- The monomer was protected with an acetonide group to reduce the chance of side reactions during polymerisation. (2)





- Deprotection of the dopamine side chains can be achieved using mildly acidic conditions.
- The ratio of ADMA to comonomer has been varied to assess the impact on adhesive properties.

## 5. ADMA containing terpolymers

i) Dopamine methacrylamide (DMA) synthesis ii) Acetonide-protected dopamine methacrylamide (ADMA) synthesis

## 3. Reactivity ratios of ADMA with MMA

- Acetonide protected dopamine methacrylamide was copolymerised with MMA to obtain reactivity ratios.
- The reactions were quenched at low conversion (< 10 %) and the monomer conversion was determined by <sup>1</sup>H NMR spectroscopy.
- The reactivity ratios of MMA  $(r_1)$  and ADMA  $(r_2)$  were calculated to be  $r_1 = 2.27, r_2 = 0.14$  (Fineman-Ross),  $r_1 = 2.34, r_2 = 0.09$  (Kellen-Tudos). This indicates that there is a preference for MMA to polymerise first in this reaction and it will be unlikely to find two ADMA units following each other.

- Terpolymers have been synthesised to enhance the versatility of the surface coatings.
- Various comonomers have been used to adjust the solubility of the polymer for various different solvent systems.
- The reactions were followed using NMR spectroscopy over 24 hours.



Stacked 1H-NMR spectra showing depletion of the monomer vinyl groups in terpolymerisation of MMA, GMA and ADMA

#### 6. Conclusions and Further Work

Acetonide-protected dopamine methacrylamide can be copolymerised, using RAFT and free radical polymerisation, with various comonomers.



Mole fraction MMA in the feed plotted against mole fraction MMA incorporated in the polymer. Straight line represents equal mole fractions in feed and polymer.

- The reactivity ratios of ADMA and MMA were found to be  $r_1 = 2.27$ ,  $r_2 = 0.14$  (Fineman-Ross),  $r_1 = 2.34$ ,  $r_2 = 0.09$  (Kellen-Tudos).
- The adhesive properties of these copolymers will be extensively studied in future work.

### **7.** References

(1) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Science 2007, 318, 426 (2) Patil, N.; Falentin-Daudré, C.; Jérôme, C.; Detrembleur, C. Polym. Chem. 2015, 6, 2919



Engineering and Physical Sciences Research Council

E: info@soficdt.ac.uk | www.soficdt.ac.uk | **f** facebook.com/softmattercdt