1. Structural Analysis

The structure of a polymer directly correlates to the properties it exhibits. Free radical polymerisation can produce copolymers with one of three structures as the monomers can assemble in a variety of ways based on their reactivity ratios (Fig. 1). For future optimisation, it is vital to firstly analyse copolymer structure.

Reactivity Ratios

The copolymer discussed in this work is a P(MMA-co-PEGMEM). A full investigation into methyl methacrylate (MMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMEM) reactivity ratios was carried out. (Fig. 2).

Fig. 1 Three example polymer structures that can be produced using free radical polymerisation where both monomers are introduced at the same time.

![Random Copolymer](Image)

![Gradient Copolymer](Image)

![Alternating Copolymer](Image)

Fig. 2. (A) Methyl methacrylate (MMA), (B) Poly(ethylene glycol) methyl ether methacrylate (PEGMEM), (C) PMMA-stat-PEGMEM

Samples from the polymerisation were analysed by 1H NMR spectroscopy. Fig. 3A shows that as time increases, surprisingly both monomers deplete at a similar rate. Analysing the data further, a graph of individual monomer depletion as a function of total conversion can be drawn (Fig. 3B). The graph shows that MMA seems to deplete slightly faster than PEGMEM.

![MMA and PEGMEM](Image)

![Monomer Conversion %](Image)

Fig. 3. (A) Stacked 1H NMR spectra of MMA and PEGMEM vinyl proton peaks depleting as a function of time, (B) Monomer in feed (M/Ma) as a function of total reaction conversion.

From this, reactivity ratio data can be determined (Table 1). The structure of P(MMA-co-PEGMEM) is a near random polymer, where the monomers have little preference for self- or cross-propagation.

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{\text{MMA}}$</th>
<th>$r_{\text{PEGMEM}}$</th>
<th>$r_{\text{MMA+PEGMEM}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman-Ross</td>
<td>1.22</td>
<td>0.63</td>
<td>0.77</td>
</tr>
<tr>
<td>Kelen-Tudos</td>
<td>1.17</td>
<td>0.60</td>
<td>0.70</td>
</tr>
</tbody>
</table>

2. Dispersion Testing

Copolymers synthesised by free radical and RAFT polymerisation were formulated with trioctyl, antifoam, wetting agent and water.

Dispersion Analysis

a. Copolymers with different $M_n$ seem to perform the same. Different $M_n$ in this range, does not seem to impact performance.
b. MMA is needed for the polymer to adsorb to the particle. Without it the particles are not wetted and cream to the top of the sample.
c. More than 60 mol% MMA is needed to allow the polymer to adsorb onto the particle.
d. pH 1 and 13 samples sediment quickly, and pH 3 and 11 perform suboptimally. This is due to screening of the electrical double layer, by ions in solution, which surrounds the particles. Optimal pH for the polymer to perform is between 5 and 9.

3. Future Work

Impact of PEG Length

Block Copolymers

Adsortion Studies

Zeta Potential Measurements

Stability behaviour of the colloidal dispersion

Which Structure is Best?

References

2. T. Kelen, E. Tudos, B. Turcsanyi, Polymer Bull. 1980, 2, 71-76

Acknowledgements

I would like to thank CRODA, Durham University and the EPSRC for the funding that is making this research possible.