Polymers for Solid Dispersion

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Introduction

Copolymers are of great interest as they offer a blend of properties that cannot be accessed with homopolymers alone. Using controlled polymerisation techniques a variety of copolymer structures can be created, leading to an even wider breadth of accessible properties. Determining monomer sequence distribution and estimating reactivity ratios in copolymerisation is important for understanding the correlation between molecular structure and macroscopic properties. Polymers are used as surfactants in solid dispersion to inhibit coagulation, flocculation and crystal growth of active ingredients.

1. Structural Analysis

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2. Dispersion Testing

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.



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

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 out¹⁻³ (Fig. 2).

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



c. Impact of Monomer Mol%

P(MMA-*stat*-PEGMEM)

 $M_n = 17,500 \text{ gmol}^{-1}$

P(MMA-stat-PEGMEM)

 $M_n = 15,400 \text{ gmol}^{-1}$

b. Impact of MMA





CRODA

EPSRC

Polymer

Analysis

New Polyme

Synthesis

Performance

Analysis



d. Impact of pH





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

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.



Dispersion Analysis

- 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 suboptimal. 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.



Figure 3. (A) Stacked ¹H NMR spectra of MMA and PEGMEM vinyl proton peaks depleting as a function of time, (B) Monomer in feed (M/M_0) 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 <u>random</u> polymer, where the monomers have <u>little preference</u> for self- or cross propagation.

Table 1. Reactivity ratios of MMA and PEGMEM.

Method	r _{mma}	r _{pegmem}	r _{mma} , r _{pegmem}
Fineman-Ross	1.22	0.63	0.77
Kelen-Tudos	1.17	0.60	0.70

3. Future Work

Block Copolymers

Zeta Potential Measurements

Stability behaviour of the colloidal dispersion

Which Structure is

References

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