Polymer Communication

# The inclusion of $\beta$ cyclodextrin provides a supramolecular solution to the problem of polymerization of dodecyl and octadecyl methacrylates in aqueous emulsion

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**Abstract**

Emulsion polymerizations of dodecyl and octadecyl methacrylate were carried out using a conventional water soluble initiator and sulphonate surfactant in the presence of $\beta$ cyclodextrin. For the first time stable latices that were taken to high conversion of monomer were produced. It is thought that $\beta$ cyclodextrin enhances the water solubility of these highly water insoluble monomers, so that the ease of transport of the monomer across the aqueous phase to the loci of polymerization is improved. Absence of sulphonate surfactant resulted in gross coagulation during polymerization. © 1999 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The emulsion polymerization of highly hydrophobic monomers such as octadecyl methacrylate (OM) and dodecyl methacrylate (DM), in aqueous media is generally not feasible using traditional surfactant systems. This is in sharp contrast to the ease of polymerizability, by emulsion methods, of the sparingly soluble homologues with shorter alkyl chains such as butyl and methyl methacrylate. The difficulty is usually considered to be a consequence of the very low water solubility of OM and DM. The monomer must display some degree of water solubility in order that the essential process of monomer transport through the aqueous phase may occur [1]. We have therefore searched for methods of increasing the water solubility of these monomers. One useful method for increasing the water solubility of organic compounds is to use cyclodextrins (CD) to form inclusion compounds with the guest hydrophobic species [2,3]. We have therefore investigated the use of $\beta$-cyclodextrin in emulsion polymerization of OM and DM and here report the first successful emulsion polymerizations of these monomers that do not involve the use of excessive levels of surfactant.

## 2. Experimental

### 2.1. Materials

The inhibitor was removed from DM (Lancaster Synthesis) and OM (containing ~35% cetyl methacrylate) (Aldrich) by washing with 2% aqueous sodium hydroxide. Both monomers were dried (over calcium chloride). The OM was used as dried. The DM was redistilled under reduced pressure prior to use. $K_2S_2O_8$ (Aldrich) and $\beta$-cyclodextrin monohydrate (CD) (Avocado) were used as supplied. Dowfax 2A1 surfactant (DOW) was a 45% wt.% aqueous solution of mono and didodecyl disulphonated diphenyl oxide, sodium salt. It was used as supplied. Deionised water was used throughout.

### 2.2. Preparations of lattices

Batch emulsion polymerizations of OM and DM were carried out. Water (200 cm³), potassium hydrogen phosphate (0.2 g) and, if required, Dowfax 2A1 (2.5 cm³) were first charged into a flanged flask under a blanket of nitrogen. This mixture was then mechanically agitated with a glass stirrer and heated to 70°C. The required amount of CD was then added. The monomer was added slowly through a dropping funnel over several minutes. The polymerization was then initiated by the addition of potassium persulphate (0.5 g). After 16 h, the polymerization was terminated by

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Table 1
Characterization results for polymerizations conducted in the presence of CD

| Refs. | Monomer | CD/g | $M_n$/kg mol$^{-1}$ | PD | Theoretical Solids/% | Coagulum/% | Average particle size/nm | Final conversion/% |
|-------|---------|------|---------------------|-----|----------------------|------------|--------------------------|--------------------|
| [1] | DM | 0.0 | 153 | 3.7 | 22 | > 50[a] | na | Na |
| [2] | DM | 1.5 | 183 | 5.4 | 22 | 33 | 278 | 93 |
| [3] | DM | 3.0 | 204 | 5.4 | 22 | 9 | 391 | 95 |
| [4] | DM | 6.0 | 235 | 4.9 | 22 | 3 | 591 | 95 |
| [5] | DM | 6.0 | 296 | 4.7 | 44 | 10 | 340 | 96 |

[a] Reaction 1 is a conventional preparation, more than 50% of the reaction mixture coagulated in the reaction vessel and the remaining monomer mixture phase separated on standing on the bench. Measurement of conversion of monomer and particle size were therefore not attempted.

cooling the reaction vessel in ice. The latex was filtered and any coagulum present was dried under vacuum and weighed.

## 2.3. Characterization

### 2.3.1. Molecular weight measurements

Molecular weights and molecular weight distributions of polymers were measured by size exclusion chromatography (SEC). Three Styragel™ 5 μm mixed gel columns (Polymer Laboratories) and a refractive index detector were used. The calibration was carried out using polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 cm$^3$ min$^{-1}$. Sample concentrations were approximately 2 g dm$^{-3}$. The SEC was also used to measure the final degree of conversion of the monomer at the end of the reaction. In these measurements the final latex rather than the isolated polymer was dissolved in THF. The chromatograms from these solutions show clear peaks due to the

presence of both polymer and residual monomer. Comparison of the relative areas of these peaks gives trivially the degree of conversion, assuming that the refractive index increments for polymer and monomer are similar. This latter assumption then means that the quoted conversions are nominal conversions.

### 2.3.2. Particle size measurements

Particle sizes of all the lattices were obtained by photon correlation spectroscopy using a Coulter N4, sub-micron particle size analyser.

## 3. Results

Table 1 shows the results of the characterization of all the latex preparations. Initially a conventional emulsion polymerization was attempted with DM as the monomer, using a sulphonate surfactant system. (reaction 1) This reaction produced over 50% of the charged monomer in the form of coagulum. While the rest of the polymer/monomer mixture that resulted was initially colloidally stable, the latex settled on standing on the bench. On addition of CD successful emulsion polymerization was achieved. Thus, in polymerizations 2, 3 and 4, which were all carried out at the same solids content as reactions 1 described above, stable lattices resulted. The lattices appeared to be indefinitely stable, that is they did not coagulate after six weeks standing on the bench at ambient temperature. However, in the case of polymerization 2 small amounts of coagulum did appear after six weeks. Conversions after 16 h were very high but the polymerizations did not go to completion. Similar polymerizations with butyl methacrylate have been shown to give 100% conversion of monomer after 3 h [4]. The molecular weight distributions were found to be unimodal. The SEC chromatograms are shown in Fig. 1. Also shown in Fig. 1 are the peaks, which correspond to residual monomer. The latex particle sizes were observed to increase as CD concentration increased, also the molecular weight averages increase with increasing CD concentration. Both the above observations strongly suggest that the main role of CD in these polymerizations is to aid the transport of monomer to the loci of polymerization. Thus, assuming that $k_t$ and
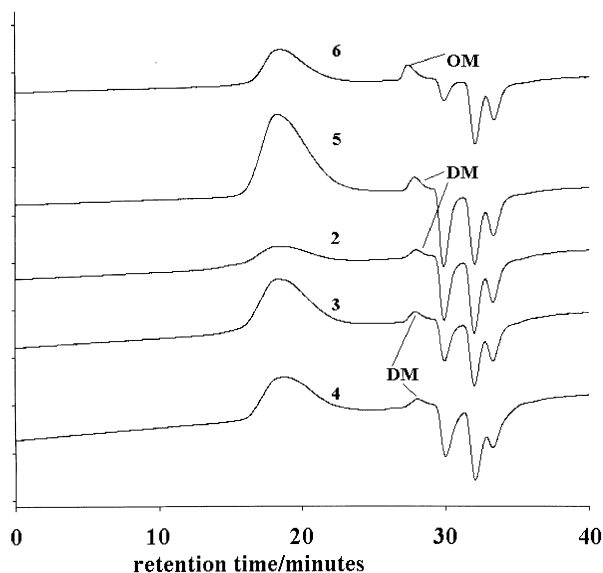


Fig. 1. SEC chromatograms of polymerizations conducted in the presence of CD, showing also the peak due to residual monomer: enumeration refers to the references in Table 1.

$k_p$ are not affected by CD concentration, the effect of increasing the amount of CD in the reaction mixture must be to increase the rate of propagation by increasing the concentration of DM at the locus of polymerization. The increase in particle size with increasing concentration of CD may be a consequence of complexation of surfactant by CD. However, the amount of coagulum also decreases as CD concentration increases, so that the increase in particle size may merely reflect the amount of suspended material. Clearly, CD in these systems does not appear to have a major role in providing colloidal stability to the particles. If CD was contributing to the colloidal stability one should expect increasing CD concentration to decrease the latex particle size. Surprisingly, increasing the solid content of the latex produced a latex of smaller average particle size. In order to further examine the role of CD, Run 4 was repeated in the absence of sulphonate surfactant. This reaction produced polymer but the latex coagulated during the reaction. Thus, in these systems both conventional surfactant and CD are required. A final polymerization was carried out in which OM, another monomer that is very difficult, if not impossible, to polymerize by emulsion means, was examined. The final entry in Table 1 shows the results from this polymerization. Inclusion of CD also produced a stable colloid of poly(octadecyl methacrylate) nanoparticles. The final conversion of monomer, however, was found to be slightly lower than in the similar DM polymerization.

## 4. Conclusion

We have shown for the first time that it is possible to prepare stable latices of the highly hydrophobic monomers, DM and OM. The use of CD as a means of increasing the water solubility of these monomers appears to aid transport across the aqueous phase. CD does not in these systems provide colloidal stability to the final latex; thus it is necessary also to incorporate a conventional surfactant.

## Acknowledgements

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