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Emulsion polymerizations in the presence of β-cyclodextrin

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Abstract

Poly(butyl methacrylate) particles were prepared using an emulsion polymerization procedure with β-cyclodextrin (β-CD) in place of the surfactant. The rate of polymerization was lower than in the equivalent sulphate surfactant stabilized emulsion polymerizations. Particle size and molecular weight distributions were unimodal and did not show any dependance on β-CD concentration. However, the average molecular weight was, in all β-CD containing polymerizations, significantly higher than in polymerizations in the absence of both surfactant and β-CD. β-CD had little effect on the behaviour of surfactant-containing systems. A tentative explanation, involving the enhancement of colloidal stability by poly(butyl methacrylate) included by β-CD amphiphilic polymers, is proposed.

Keywords: Emulsion polymerization; Inclusion compound; Poly(butyl methacrylate)

1. Introduction

Cyclodextrins (CDs) are well known cyclic species that can solubilize hydrophobic compounds in aqueous media [1]. The solubilization is effected by complexation of the water-insoluble species within the hydrophobic cavity of the CD. The outer hydrophilic surface then interacts with water to maintain the solubilization of the complex. While many studies on the solubilization of low molecular weight and polymeric species are available [2], very little is known of the behaviour of heterogeneous polymerization reactions in the presence of CDs. Although recent reports on the use of CDs and other non-cyclic polymers, capable of forming inclusion compounds, in copolymerizations of hydrophobic monomers with water soluble monomers have appeared in the patent literature [3–5]. Several polymerizations conducted in the presence of CDs have given rise to main chain rotoxane polymers that are made water-soluble by the CD ring [6–9]. Heterogeneous polymerizations, such as emulsion and suspension polymerizations, are frequently used techniques for the preparation of high molecular weight polymers. Surfactants, often alkyl sulphates or mixtures of ionic and non-ionic amphiphiles, can often be essential in these processes. These surfactants impart either electrostatic or entropic stability to the dispersion [10]. Polysaccharides as well as synthetic polymers are also used as colloid stabilizers. Derivatized cellulose has, for example been used to impart stability. For example, recently Chern et al. [11] reported the use linear high molecular weight dextran in emulsion polymerization. This material imparted entropic stabilization to the colloid. Grafting of methyl methacrylate to radicals formed by abstraction of hydroxyl hydrogens ensured that segments of the dextran chain were adsorbed on the particle surface. Hydroxyethyl-modified cellulose can also act as a coagulating or thickening agent in acrylic latices, or as a stabilizing agent in vinyl acetate latices [12–14]. Grafting of monomers to the cellulose also plays an important role in these systems. The mechanism of stabilization with these macromolecular stabilizers is usually thought of as entropic in origin. Clearly, if the macromolecule is to stabilize the colloid, the system must gain enough entropy to overcome the very large amounts of enthalpy associated with the high surface area of a polymeric colloid. As solvated segments of a polymer chain can exist in many random coil conformations the required increase in the entropy of the surface can be supplied by a macromolecular stabilizer that contains hydrophobic segments adsorbed to the particle surface and also segments that are soluble in the aqueous phase. Adsorption is usually promoted by using amphiphilic polymers with block or graft architectures. Moreover, charged amphiphiles, such as alkyl sulphates, stabilize the colloid by electrostatic repulsion. With these stabilizing mechanisms (entropic or electrostatic) in mind one would not expect a rigid non-charged cyclic polymer such as CD to act as a

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Table 1
Formulation, molecular weight (SEC, in THF) and particle size (photo correlation spectroscopy) data for the polymerizations of BMA (All polymerizations proceeded to 100% conversion of monomer over the reaction period)

Run	BMA/g	Water/cm^{-3}	DPOS-45/g	CD/g	M_n/kg mol^{-1}	M_w/M_n	PS[a]/nm
1	80	200	1.7	0	673	3.2	120
2	80	200	1.7	0.4	532	3.4	105
3	80	200	1.7	1.6	622	3.0	107
4	80	200	0	0	31	8.3	Coagulated
5	80	200	0	0.4	33	9.7	493
6	80	200	0	1.6	71	4.4	730
7	80	200	0	1.6	107	4.0	614
8	60	200	0	1.6	145	4.2	607
9	60	250	0	0.0	38	12.5	1000[b]
10	60	250	0	1.6	142	5.0	652
11	60	250	0	3.2	131	3.8	801
12	60	250	0	4.8	156	5.2	574
13	60	250	0	6.0	103	6.4	526

[a] Particle size.

[b] Particle size of the latex, however 50% of the material was produced as coagulum.

colloid stabilizer. However, during our work on functional polymer colloids [15,16] we have surprisingly discovered that the CD can stabilize some polymer colloids. As far as we are aware no work on the effect of the cyclic polysaccharides on dispersion polymerization has been published. However, Jeromin and Ritter [17], reported recently the polymerization of cyclohexyl methacrylate and phenyl methacrylate in either chloroform or water in the presence of a methylated CD. In that work, aqueous CD/monomer complexes were found to be homogeneous. Upon polymerization the polymer precipitated from the solution so that the system became heterogeneous. This article presents the first results of our work in this area and outlines a tentative hypothesis for the colloid stabilization mechanism.

2. Experimental

2.1. Materials

The inhibitor (hydroquinone monomethyl ether) was removed from butyl methacrylate (BMA) (Aldrich) by washing with 2% aqueous sodium hydroxide The monomer was then dried over calcium chloride and distilled under reduced pressure. $K_2S_2O_8$ was recrystalized from water. β-cyclodextrin monohydrate (β-CD) (Avocado) was used as supplied. Dowfax 2A1 surfactant (Dow Chemicals) was a 45% w/w aqueous solution of mono and didodecyl disulphonated diphenyl oxide, sodium salt; it was used as supplied. Deionised water was used throughout.

2.2. Preparation of latices

Batch emulsion polymerizations of BMA were carried out. The latex formulations are given in Table 1. Water, potassium hydrogen phosphate (0.2 g), β-CD and, if required, Dowfax 2A1 were first charged to a flanged flask under a blanket of nitrogen. This mixture was then mechanically agitated at 70°C. The monomer was added slowly through a dropping funnel over several minutes and the system allowed to equilibrate in the vessel for 30 min. The Polymerization was then initiated by the addition of potassium persulphate (0.5 g). The polymerization was sampled at various times. These samples were then quenched by the addition of hydroquinone. The conversion of monomer was established by determining the solid contents of the samples. After 6–8 h, the polymerization was terminated by cooling in ice. The latices were then filtered through glass wool and characterized by determining the average particle sizes, solid contents and molecular weights.

2.3. Molecular weight measurements

Molecular weights and molecular weight distributions of polymers were measured by size exclusion chromatography (SEC). Three Styragel™ 10 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}.

2.4. Particle size measurements

Particle sizes of all the latices were obtained by photon correlation spectroscopy using a Coulter N4, submicron particle size analyser. Some of the latices were also characterized by transmission electron microscopy (TEM) using a JEOL GEM 100CX. The latex was first pipetted onto a copper TEM grid and them air dried before examination.

2.5. Solid contents

Solid contents were determined gravimetrically. Thus, a

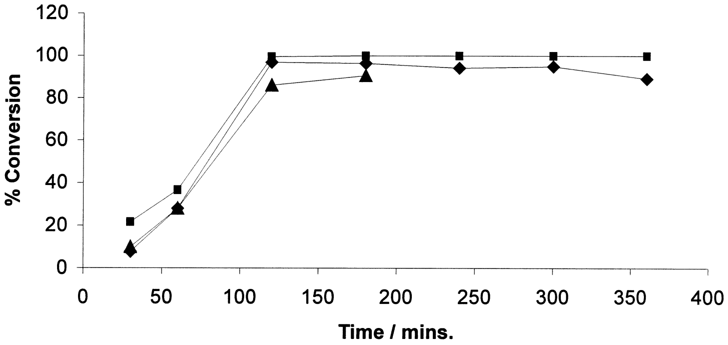

Fig. 1. Conversion versus time plots for BMA polymerizations reactions in the presence of β-CD at β-CD concentrations of: ◆ 5.64 mmol dm^{-3}, ■ 16.92 mmol dm^{-3}, ▲ 21.15 mmol dm^{-3}.

sample of the latex was weighed out on an aluminium foil dish. Further, polymerization of the residual monomer was prevented by the addition of a weighed amount of hydroquinone. The sample was then air dried to constant weight at 90°C. Each determination was carried out in triplicate and the average of the three determinations recorded.

3. Results

3.1. Addition of β-CD to an emulsion polymerization of BMA stabilized by sulphate surfactant

Initially, CD was added to a sulphate-stabilized emulsion polymerization of BMA. The formulations are given in Table 1 (reactions 1–3). The effect on the rate of polymerization was negligible, all polymerizations being essentially complete after 30 min at 70°C. Also, little change in the final molecular weight average (M_n) or particle size was observed. From these observations it is clear that, while β-CD may complex hydrophobes within this system, these complex structures have little effect on the course of the emulsion polymerization in the presence of sulphate surfactant.

3.2. Addition of β-CD to a dispersion polymerization of BMA in the absence of surfactant

Following on from the aforementioned experiments, polymerizations were carried out in the absence of surfactant. The results for the various polymerization recipes are shown in Table 1 (reactions 4–13). Initially a control polymerization was carried out. This reaction (reaction 4) contained neither surfactant nor β-CD and coagulated at an early stage in the polymerization. As can be clearly seen from these results, the addition of β-CD had a beneficial effect on the colloidal stability of the products. In reactions carried out at the monomer (solids) content of 28.5% w/w. (reactions 5–7), large amounts of product coagulated from the reaction mixture. However, unlike in the control experiment, a proportion of the polymer was present as a stable colloid. The fraction of polymer, which was observed as a stable colloid was 25 and 70% w/w, respectively, for reactions 5 and 6/7. As can be observed from Table 1 increasing the β-CD concentration gave an increase in molecular weight. However, from these limited experiments, it can be inferred that the molecular weight increase is not a simple function of CD concentration. Thus, little change is observed on increasing the CD concentration from 0 mmol dm^{-3} of aqueous phase (reaction 4) to 1.8 mmol dm^{-3} of aqueous phase (reaction 5), but the molecular weight increases by a factor in excess of two on raising the concentration further to 7.1 mmol dm^{-3} of aqueous phase (reactions 6 and 7). In order to confirm this observation the reaction at a CD concentration of 7.1 mmol dm^{-3} of aqueous phase was repeated. While the molecular weights from the reactions 6 and 7 differ, both were significantly higher than the molecular weights obtained from reactions 4 and 5. Owing to the gross coagulation of either all, or a fraction of the reaction mixture, it was not possible to obtain reliable rate data. However, an enhancement of the rate was inferred from the observation that at 0 and 1.8 mmol dm^{-3} of aqueous phase the total amount of polymer formed after 300 min corresponded to approximately 15% conversion of the monomer. Whereas, at the higher β-CD concentration of 7.1 mmol dm^{-3} of aqueous phase, 75% of the monomer had been converted in this time. Interestingly, the polymerizations carried out at a β-CD concentration of 7.1 dm^{-3} of aqueous phase gave large regular particles of diameters circa 1 mm as well as the smaller stable latex particles.

In the next set of polymerizations we attempted to minimize the amount of coagulum formed by reducing the solid content of the latex. The amount of material that was produced in colloidal form increased to values approaching 100% on reducing the solid content of the latices to approximately 19% w/w. Thus, polymerizations 8–13 gave latices containing very little coagulum. In contrast to conventional emulsion polymerizations, which usually show a strong dependence of particle size on surfactant concentration, the particle sizes from these polymerizations appear to be independent of β-CD concentration. Thus, as Table 1 shows, all of these formulations gave latices with particle diameters circa 500–800 nm, with no clear relationship

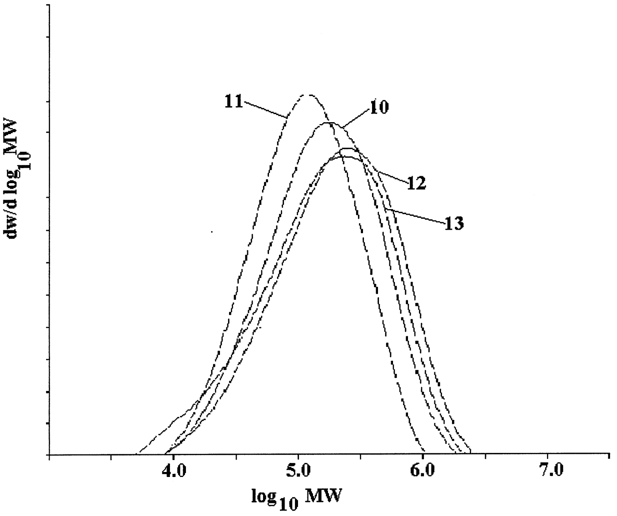

Fig. 2. Molecular weight distributions of polymers produced in the presence of β-CD.

between β-CD concentration and particle size. Conversion time plots for some of these reactions are shown in Fig. 1.

It was also noticed that the storage stability of the latex increased with increasing β-CD concentrations; latices with lower CD concentrations displayed some settling over time whereas, those with higher CD concentration remained well dispersed. Particle size distributions were either unimodal or, in some cases, bimodal. Molecular weight distributions were also unimodal with polydispersities between 4.0 and 6.5. Molecular weight distributions from reactions 10 to 13 are shown in Fig. 2. Of note is the fact, that these stable latices gave lower polydispersities and higher Mn than materials produced using the higher solid content and less stable formulations.

An outstanding feature of these polymerizations is that, in some cases, rather narrow particle size distributions were obtainedd. An example of a TEM obtained from latex 13 is shown in Fig. 3.

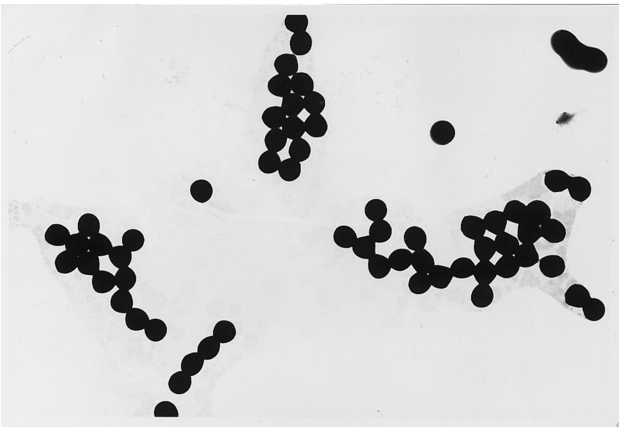

Fig. 3. TEM micrograph of latex 13 (magnification = 10 0000 ×).

4. Discussion

It would appear from the aforementioned results that the β-CD can play an important role in increasing colloid stability and the rates of polymerization in emulsion polymerization of BMA. The enhancement of the rate is evidenced by the increase in number average molecular weight and rate of polymerization over that observed in the absence of β-CD. However, the effect is not a simple function of β-CD concentration in that neither the rate of polymerization nor the particle size alter much with further increase in β-CD concentration. As we have pointed out in the introduction, a rigid cyclic molecule would not normally be expected to impart stability to a colloid. A new type of colloidal stabilization may thus be operative in these polymerizations. The rates of polymerization never reach those observed in the surfactant-containing system nor does the addition of β-CD have an effect on the surfactant-containing polymerizations. A possible explanation, which builds upon accepted current theories of emulsion polymerization, may be as follows. At the start of the polymerization β-CD may complex a fraction of the BMA monomer, so that the concentration of monomer in the aqueous phase will be higher than in the absence of β-CD. This will have the effect of increasing the rate of initiation and thus the overall rate of polymerization. In the absence of dethreading, the polymer produced from this process may be a rotoxane with a PBMA centre and CD collars. However, Ritter [14] has shown that in a similar study some dethreading does occur during polymerization. This dethreaded CD will thus be available for further complexation of monomer. As the molecular weight of the polymer increases, some β-CD may become dethreaded and this will cause the growing polymer radical to precipitate. It is possible that this material will then enter a monomer droplet and may continue to propagate until termination occurs. Alternatively, precipitation may result in the formation of particles that act as new loci for polymerization. In this case, β-CD will have a further role in that the enhanced solubility of the monomer will allow fast diffusion of monomer to these newly formed loci. In this scenario, if diffusion of monomer were rate limiting, the rate of propagation would be increased. In both situations one would expect to observe an increase in molecular weight as a consequence of the reduced frequency of collisions between macroradicals. That is, in both cases, after precipitation of the growing polymer chain, termination can only occur when a second radical enters the polymerizing particle.

If a fraction of the β-CD remains threaded on the PBMA chain then the polymer will have amphiphilic character. That is PBMA segments that are included will display hydrophilic behaviour while those segments that are not included will be hydrophobic in nature. These polymers may then be able to act as steric stabilizers. At this point we must stress that this explanation is rather tentative; further work is necessary and is currently underway. Other aspects that, have not, as yet, been addressed include the extent of grafting onto β-CD and β-CD chain scission, both of which are also expected to be significant.

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