# Cyclodextrins in Polymer Synthesis: A Simple and Surfactant Free Way to Polymer Particles Having Narrow Particle Size Distribution

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ABSTRACT: The free radical polymerization of styrene or methyl methacrylate under semicontinuous conditions in water in the presence of randomly methylated-$\beta$-cyclodextrin (RAMEB) is described. The polymerization reactions were carried out in water with potassium peroxodisulfate as free radical initiator at 80 °C in the presence of different amounts of cyclodextrins. Compared to batch polymerizations, where the water-insoluble polymer precipitates or produces high amounts of coagulum, this new method results in quantitative conversion of the monomers and leads to stable latexes with nearly monodisperse polymer particle size distributions, which are very useful in many technical applications.

## Introduction

Cyclodextrins (CD's) are cyclic oligoamyloses, consisting of 6 (α), 7 ($\beta$), 8 ($\gamma$), or 9 ($\delta$) units of 1,4-linked glucose. They exhibit a torus-shaped structure with a hydrophobic cavity and a hydrophilic outer side. Because of this structure, they are able to enclose smaller hydrophobic molecules to form host−guest compounds, where the hydrophobic guest molecule is encapsulated by the cyclodextrin.[1−4] The outer hydrophilic surface then interacts with water in order to maintain the solubilization of the complex. This inclusion phenomenon leads to significant changes of the solution properties and reactivities of the guest molecule. Water-insoluble molecules become water-soluble on treatment with aqueous solutions of cyclodextrins without any chemical modification of the guest molecule, because there are no covalent bonds formed by the host−guest interaction of the CD and the water-insoluble molecule.

In our group, we recently have investigated the surfactant free batch polymerization in water of 1:1 (molar) CD complexed vinyl derivatives and some other types of monomers under free radical,[5−13] controlled "living" radical,[14] and for the synthesis of conducting polymers under oxidative conditions[15,16] from aqueous media. There, we obtained high monomer conversions in short reaction times and the polymers could be easily isolated by simple filtration. The emulsion polymerization of vinyl compounds, using CD's in combination with anionic emulsifiers, has been described.[17,18] Rimmer and Tattersall reported about the batchwise emulsion polymerization of *n*-butyl methacrylate in the presence of $\beta$-CD;[19] in some cases he made use, besides CD, of an anionic surfactant. Madison and Long investigated the batch polymerization of methacrylic monomers which where complexed by methylated $\beta$-CD.[20] The emulsion polymerization of methacrylates in the presence of cyclodextrins in combination with surfactants has been described by Lau.[21] However, batchwise polymerization leads often to considerable amounts of coagulum which is unwanted in the synthesis of stable latexes. Also it will become clear that additional anionic surfactants are undesirable in view of the objects to be attained. Moreover, all the above-mentioned reports are related with the use of CD's in heterogeneous reactions, wherein polymer particles having a heterogeneous particle size distribution (PSD) are obtained, whereas use of polymer particles having a narrow particle size distribution are highly desired. Some methods of producing latexes[22−24] or polymer particles[25−28] having uniform particle size distribution have been described. Preparation of monodisperse latexes is important, e.g., in coating applications, since the PSD influences film formation and shear stability. For graphical applications this is important in because latexes are used as a binder in backing layers, in emulsion layers, in adhesive layers and in top coatings. Monodisperse PSD's are moreover important when latexes are used in inks. For ink-jet inks, the jetability will also depend on the PSD. Another quite novel application is the use of monodisperse particles in the preparation of photonic crystals.[29−31] Periodic superstructures diffract electromagnetic radiation if the lattice constant matches the wavelength of light. Well-ordered three-dimensional photonic crystals based on polystyrene particles are known. PMMA particles can also be used and have the advantage to be suitable for use as an electron-beam resist.

Thus, it was an intention of our present work to make use of CD's in heterogeneous polymerization reactions in water, to obtain latexes with narrow PSD.[32]

## Results and Discussion

In our previous reports, we have investigated the batch polymerization of 1:1 (molar) complexed hydrophobic monomers in water. There, the polymers could be synthesized in very high yields after very short reaction times and isolated by simple filtration. However, for other applications which have been mentioned before, the polymers should be obtained as stable latexes. Moreover, a narrow PSD is also desirable. Now, in this report we have investigated the polymerization

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**Table 1. Overview of the Reaction Parameters and Results of the Polymerization of Styrene under Semicontinuous Conditions in the Presence of Different Amounts of Randomly Methylated *β*-Cyclodextrin (RAMEB) (2 h at 80 °C, Then 1 h at 85 °C)**

| polymer **3** | RAMEB (g) | water (g) | $K_2S_2O_8$ (g) | styrene (g) | $M_n$ (g/mol) | PD | APS (nm) | PSD |
|---|---|---|---|---|---|---|---|---|
| **a** | 0 | 50 | 0.05 | 4.5 | 62 000 | 6.46 | 403 ± 16 | broad |
| **b** | 0.25 | 50 | 0.05 | 4.5 | 41 000 | 4.02 | 358 ± 2 | narrow |
| **c** | 0.5 | 50 | 0.05 | 4.5 | 33 000 | 3.07 | 267 ± 3 | narrow |
| **d** | 1.0 | 50 | 0.05 | 4.5 | 39 000 | 2.77 | 318 ± 2 | narrow |

**Scheme 1. Polymerization of Styrene or MMA under Semicontinuous Conditions in the Presence of Different Amounts (wt % to the Monomer) of Randomly Methylated *β*-Cyclodextrin (RAMEB)**

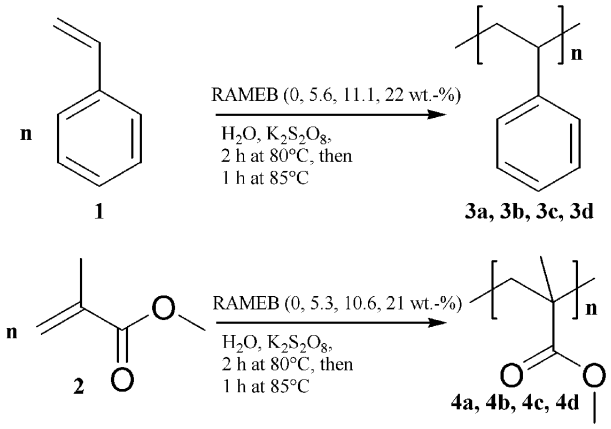



**Table 2. Overview of the Reaction Parameters and Results of the Polymerization of MMA under Semicontinuous Conditions in the Present of Different Amounts of Randomly Methylated *β*-Cyclodextrin (RAMEB) (2 h at 80 °C, Then 1 h at 85 °C)**

| polymer **4** | RAMEB (g) | water (g) | $K_2S_2O_8$ (g) | MMA (g) | $M_n$ (g/mol) | PD | APS (nm) |
|---|---|---|---|---|---|---|---|
| **a** | 0 | 50 | 0.05 | 4.7 | 32 000 | 2.2 | 292 ± 3 |
| **b** | 0.25 | 50 | 0.05 | 4.7 | 31 000 | 2.13 | 297 ± 11 |
| **c** | 0.5 | 50 | 0.05 | 4.7 | 37 000 | 2.06 | 517 ± 15 |
| **d** | 1.0 | 50 | 0.05 | 4.7 | 32 000 | 2.28 | 588 ± 24 |

behavior of styrene (**1**) and MMA (**2**) under semicontinuous conditions in the presence of different amounts of RAMEB in water, initiated with potassium peroxodisulfate (Scheme 1). Flasks were charged with water and different amounts of RAMEB were added.(Tables 1 and 2). Also, comparative experiments without RAMEB were performed. After that, the solutions were heated to 80 °C, degassed with nitrogen and the initiator was added. Then, the monomers were constantly added via syringes over a period of 2 h. After the monomer additions were completed, the solutions were heated at 85 °C for one additional hour to ensure quantitative monomer conversions.

At the beginning of the reaction (styrene addition) one could observe that the samples with CD (**3b**, **3c**, and **3d**) showed already after 4 min a blue opalescence, whereas the sample without CD (comparative example **3a**) started to show an opalescence only after 10 min. The higher the CD concentration in the reaction mixture was, the sooner the samples became milky turbid. This was already visualized after 10−15 min by all CD-containing batches. The run without CD **3a** was much slower to become a turbid dispersion and then only after approximately 35 min.

Using these conditions, very stable latexes of polystyrene **3a**, **3b**, **3c**, and **3d** were obtained. It was obvious that the polydispersities (PD) of the polystyrene latexes

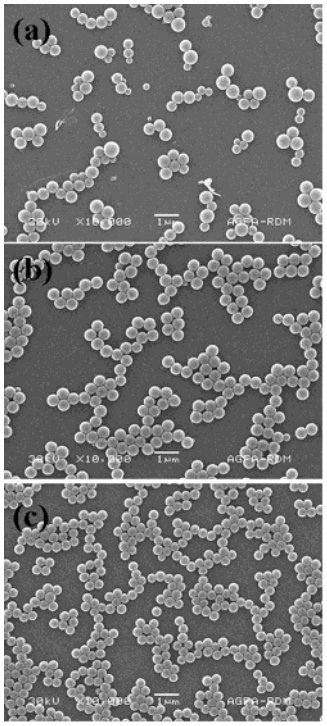



**Figure 1.** SEM image of polystyrene particles, obtained: (a) comparative example **3a** (0 wt % cyclodextrin), broad particle size distribution; (b) **3b** (5.6 wt % cyclodextrin), narrow particle size distribution; (c) **3c** (11.1 wt % cyclodextrin), narrow particle size distribution.

**3b**, **3c**, and **3d**, prepared in the presence of CD, were much smaller than in the comparative example **3a** that was prepared without CD (Table 1). The average particle sizes (APS) decreased with increasing CD concentration from latex **3a** (403 nm) via **3b** (358 nm) to **3c** (267 nm) and increased with sample **3d** (318 nm). The main point was, however, that the latexes **3b**, **3c**, and **3d**, prepared in the presence of CD, showed a very narrow PSD in contrast to sample **3a** which was synthesized without CD. Figure 1a shows the SEM image of the comparative example **3a** (0% CD in the reaction mixture) which shows a very broad PSD. Parts b and c of Figure 1 show the SEM images obtained from samples (polymerized in the present of CD) **3b** and **3c**, respectively, and prove the narrow PSD.

The monomer is added semicontinuously to the reaction vessel. This gives a high initial CD/monomer ratio, which enables fast complexation. This complexes can become polymerization sites or loci. Furthermore, no or hardly any monomer droplets are present. It is proposed that the CD−monomer complexes become polymerization sites where micellar nucleation occurs. Whereas in the absence of CD only homogeneous nucleation occurs, micellar nucleation also becomes important now. CD, in all steps of the preparation method, clearly contributes to an improvement of the colloidal stability of the particles: formation of stable micelles and micellar

**Table 3. Overview of the Reaction Parameters and Results of the Polymerization of *n*-Butyl Methacrylate under Batch- and Semicontinuous Conditions in the Presence of Native *β*-Cd ($T$ = 70 °C)**

| polymer **6** | *β*-CD (g) | water (g) | $K_2S_2O_8$ (g) | BMA (g) | $M_n$ (g/mol) | PD | coagulum (wt %) | APS (nm) |
|---|---|---|---|---|---|---|---|---|
| **a**: batch | 1.6 | 125 | 0.25 | 30 | 115 000 | 4.2 | 5.1 | 717 ± 84 |
| **b**: semicontinuous | 1.6 | 125 | 0.25 | 30 | 120 000 | 2.6 | 1.4 | 657 ± 16 |

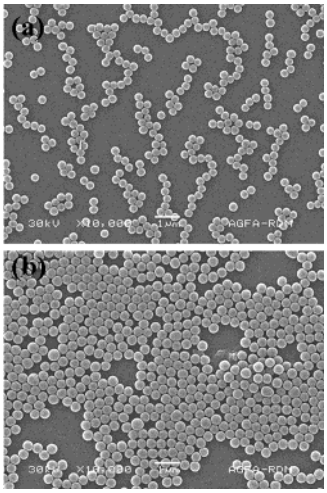


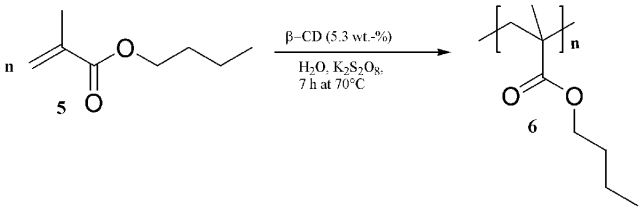

**Figure 2.** PMMA particles, obtained: (a) **4a** (no cyclodextrin); (b) **4b** (5.3 wt % cyclodextrin).

nucleation attributes to a fast nucleation and to formation of stable colloidal particles with a narrow PSD.

Also, the polymerization of MMA was, as described for styrene, carried out under semicontinuous conditions in the presence of different CD amounts (Table 2) and stable latexes were obtained. As observed with the styrene polymerization, the samples containing CD (**4b**, **4c**, and **4d**) became much earlier, after dosing the MMA, a turbid dispersion than the comparative example **4a**, which contained no CD in the reaction mixture. The PD's of the PMMA latexes, prepared in the presence of CD (**4b**, **4c**, and **4d**) were in the same order as the control experiment **4a**, synthesized in the absence of CD (Table 2). The APS however increased with increasing amounts of CD in the reaction mixture. This is in contrast to the observation made in styrene polymerization, where first the APS decreased with increasing CD amounts. This phenomenon is yet not completely understood and is subject of our further investigations.

The PSD's of the PMMA latexes **4b**, **4c**, and **4d** were narrow. However, there was not as large a difference, as observed in the styrene polymerization, with the control experiment **4a**, which was prepared without CD. Figure 2a shows the SEM image of the comparative example **4a** which contained no CD in the reaction mixture, and Figure 2b shows the SEM image of the PMMA latex **4b**, synthesized in the presence of 5.3 wt % CD. In the MMA polymerization, the influence is mainly reflected in an increase of the particle size with increasing amounts of CD in the reaction mixture. Because the monomer conversions were quantitative in all examples, the final particle size can be adjusted easily by the variation of the CD amounts without changing the other reaction parameters. However, in contrast to the styrene polymerization, the particle sizes increase by addition of CD. Significant differences in PSD, as found in the styrene polymerization, were not observed. However, it is also useful to remark that CD-complexes with MMA are not as stable as CD-complexes with the very hydrophobic styrene.[33] This could also be

**Scheme 2. Polymerization of *n*-Butyl Methacrylate in the Presence of *β*-Cyclodextrin under Batch (6a) and Semicontinuous (6b) Conditions[a]**




[a] $T$ = 70 °C; total reaction time = 7 h. In example 6b, the monomer was added via a syringe over a period of 3 h.

a reason for the significant differences found in the styrene polymerization between control experiment (no CD) and the polymerizations carried out in the presence of CD with respect to their PSD's. Styrene itself has a low solubility in water (∼0.23 g/L at 20 °C) The CD increases significantly the solubility of styrene in water. Thus, the more CD is present in the aqueous phase, the more styrene is solubilized. Because initiation occurs with a water-soluble initiator, the more nuclei are formed which give more polymer particles having a smaller particle size. As mentioned before MMA is much more soluble in water (∼12 g/L at 20 °C) than styrene. So it becomes clear that the effect of the CD on the MMA polymerization shows a different result compared to the polymerization of styrene. This was also proved via a some simple batch polymerization experiment of styrene and MMA in water, carried out at 40 °C for 2 h and initiated with the water-soluble redox initiator system $K_2S_2O_8/Na_2S_2O_5$. The styrene batch polymerization experiment, containing an equimolar amount of RAMEB had a conversion of 91% whereas the control experiment without RAMEB showed under identical conditions less than 1% conversion. Using the more hydrophilic MMA, these drastic effects were not observed; the conversions in the presence or absence of RAMEB where almost the same (∼80%).

It is remarkable that all the latexes contained no coagulum. Encouraged by this observation, we decided to follow a batch polymerization experiment of *n*-butyl methacrylate in the presence of native *β*-CD, described in the literature by Rimmer and Tanttersall[19] and compared it with a polymerization experiment carried out under semicontinuous conditions without changing the other reaction parameters (Scheme 2). The two obtained poly(*n*-butyl methacrylate) latexes (PBMA) **6a** and **6b** were investigated for their coagulum content, molecular weight, PD, and APS (Table 3). First of all, it was observed that the polymerization of BMA under batch conditions (**6a**) gave about 5.1 wt % of coagulum, whereas performance of the same reaction with semicontinuous addition of the monomer (**6b**) resulted in less than 1.4 wt % of coagulum. It was also noticed that the semicontinuous reaction gave a narrower molecular weight distribution. In this case, the CD did not effect significantly the latex sizes and molecular weights; it is more the semicontinuously addition of the monomer (example **6b**) that gives better PD and lower coagulum.

## Conclusions

It was shown from these examples that the semicontinuous procedures gave more stable latexes, compared to batch wise polymerization reactions. The cyclodextrin mediated reactions with a semicontinuous addition of the monomers gave also a much better colloidal stability of the polymer particles, Furthermore, the polymer particles had a narrower particle size distribution and lower PD's. The method we described gives a new, simple way to the synthesis of polymer particles with narrow PSD without using surfactants or solvent mixtures. The latexes can be used directly as taken from the reaction vessel without further purification steps.

## Experimental Section

Styrene (Fluka), MMA (Merck), and *n*-butyl methacrylate (Fluka) were distilled prior to use. Methylated $\beta$-cyclodextrin (RAMEB) (CAVASOL W7 M, technical grade, Wacker), $\beta$-cyclodextrin (Wacker), and potassium peroxodisulfate (Fluka) were used as received. Demineralized water was used in all experiments.

For molecular weight determinations, samples of the latexes were freeze-dried. GPC measurements of the polystyrene and PMMA samples were performed with a setup of the company PSS with THF as eluent at 25 °C. Calibration was done with polystyrene-or PMMA standards (PSS) with a molecular weight range between 374 and 1 000 000. With a flow rate of 1 mL/min, 150 $\mu$L of a 0.125 wt % polymer solution in THF was injected onto a column combination consisting of a PSS−SDV 5 $\mu$m, $10^3$ Å, 8 × 50 mm as precolumn and a set of PSS−SDV 5 $\mu$m, 8 × 300 mm with 100, $10^3$, and $10^4$ Å porosity as analytical columns. Detection of the signals was performed with a TSP UV2000 UV−vis detector (254 nm) and a modified Knauer RI detector. Indicated molecular weights of poly(*n*-butyl methacrylate) were obtained with the same setup but with chloroform as an eluent and using polystyrene standards. The evaluation was performed using PSS-WinGPC 4.01 software. Amounts of coagulum in the latexes where determined by filtrating the latex trough filter paper, drying the residue in a vacuum at 70 °C for 12 h and weighing.

Particle sizes were measured by means of light-scattering using a Brookhaven Instruments Particle sizer BI90. Scanning electron microscopy was performed with a JEOL JSM-5600 scanning electron microscope with an acceleration voltage of 30 kV. The pictures taken were obtained according to the following method: Samples of the latexes were diluted in distilled water. A drop of this solution was put on a substrate, dried, and covered with a thin gold coating and then examined.

**General Polymerization Procedure for Polystyrene (3a, 3b, 3c, 3d) and PMMA (4a, 4b, 4c, 4d) Latexes.** First, 100 mL flasks, equipped with magnetic stirring bars, were each charged with 50 mL of water. Then, randomly methylated $\beta$-cyclodextrin (RAMEB) was added in different amounts to each flask, according to the data given in Table 1 (polystyrene) or Table 2 (PMMA). The solutions were heated to 80 °C and deaerated by bubbling with nitrogen for 10 min. Then, the initiator was added, the flasks were sealed with rubber septa, and the solutions were heated under stirring for another minute. Then, 5 mL of styrene or MMA were added dropwise via syringes over a period of 2 h to the stirred (350 rpm) solutions while maintaining the temperature at 80 °C. After completion of the addition of the monomers, the reaction mixtures were heated at 85 °C for an additional hour.

**Polymerization Procedure for Poly(*n*-butyl methacrylate) 6a and 6b.** First, 250 mL flasks, equipped with magnetic stirring bars were each charged with 125 mL of water. Then, 1.6 g of native $\beta$-cyclodextrin were added to each flask. The solutions were heated to 70 °C and deaerated by bubbling with nitrogen for 10 min. For experiment **6a** the whole amount of BMA was added at once and stirred for an additional 10 min. Then, the initiator was added (see Table 3 for details) and sealed with a rubber septum while maintaining stirring (350 rpm) and heating at 70 °C for 7 h. For experiment **6b**, the initiator was added and the flask was sealed with a rubber septum and stirred for another minute. Then, the BMA was added via a syringe over a period of 3 h while maintaining stirring (350 rpm) and heating at 70 °C. After completion of the monomer addition, the reaction mixture was heated and stirred for an additional 4 h.

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(33) ‡Storsberg, J. Ph.D. Thesis, University of Mainz, Germany, 2001. The complex stabilities of styrene or MMA with RAMEB in water were determined by isothermic titration microcaloriemetrie (ITC) and UV-differences spectroscopy. It was found that the complex stability of MMA with RAMEB in water is much lower than the complex stability of styrene with RAMEB ($K_{styrene} \approx 500\ M^{-1}$, $K_{MMA} \approx 26\ M^{-1}$, $T = 25$ °C). Brief descriptions of experimental methods and results will be published elsewhere.


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