

## The Effect of Cyclodextrins in Polymer Particles Synthesis

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**Abstract:** The free radical polymerization of styrene in water in the presence of  $\beta$ -cyclodextrin ( $\beta$ -CD) is described. It is found that  $\beta$ -CD could greatly accelerate the polymerization, enhance the final conversion of monomer. The particle-size distribution of the final polymer is also improved than that without  $\beta$ -CD in the system.

**Keywords:** Cyclodextrin, polymerization conversion, polymer particles.

Cyclodextrins(CD) are cyclic oligoamyloses, consisting of 6( $\alpha$ ), 7( $\beta$ ), 8( $\gamma$ ) units of 1, 4-linked glucose. Because of their hydrophobic cavity and hydrophilic outer side, they are able to enclose smaller hydrophobic molecules to form host-guest compounds. The formation of these complexes leads to significant changes of the solubility and reactivity of the guest molecules.

Recently, there are many articles about the use of native CD or CD derivatives in polymer synthesis<sup>1-3</sup>. Most of them put the emphases on the emulsion polymerization of methacrylic monomers in the presence of CD in combination with surfactants. The surfactants influenced the polymerization greatly, so the real effect of CD on the polymerization could not be judged properly. Further more, the surfactants have disadvantages in the application of final polymer particles, such as used as medicine carrier, coatings, biomaterials, *etc.*

In this work, we took styrene as monomer, potassium peroxodisulfate as radical initiator, the reaction was carried out in water in the presence of  $\beta$ -CD without any surfactant. The influences of amount of  $\beta$ -CD and monomer on the conversion rate, and the polystyrene particle-size distribution have been studied.

### Experimental

100 mL flask was charged with 50 g of water, and different amounts of  $\beta$ -CD were added (shown in **Table 1**). The reaction mixture was degassed with nitrogen for 20 min and heated to 80 °C. The initiator was added at this temperature. The reaction was proceeded for 5 hours at 80 °C.

The particle-size distribution(PSD) and average particle size(APS) were determined

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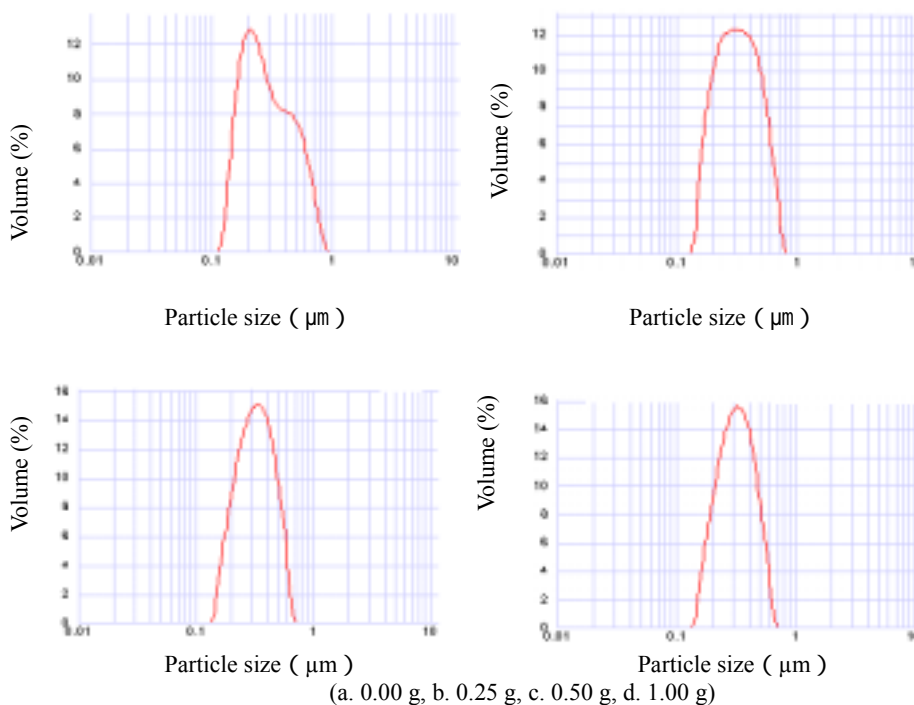
by laser diffraction particle size analyzer (Mastersizer 2000), the monomer conversion was determined by weight method<sup>4</sup>.

## Results and Discussion

**Table 1** reaction parameters and results of the polymerization of styrene in the presence of different amounts of CD ( 5 hours at 80 °C )

Polymer	$\beta$ -CD (g)	$K_2S_2O_8$ (g)	Water (g)	Styrene (g)	Final conversion(%)	APS (nm)	PSD
1	0.00	0.06	50	5.0	60.3	212	broad
2	0.25	0.06	50	5.0	71.1	300	broad
3	0.50	0.06	50	5.0	78	330	narrow
4	1.00	0.06	50	5.0	95.6	336	narrow

**Figure 1** Particle-size distribution of polystyrene in the presence of different amounts of  $\beta$ -CD



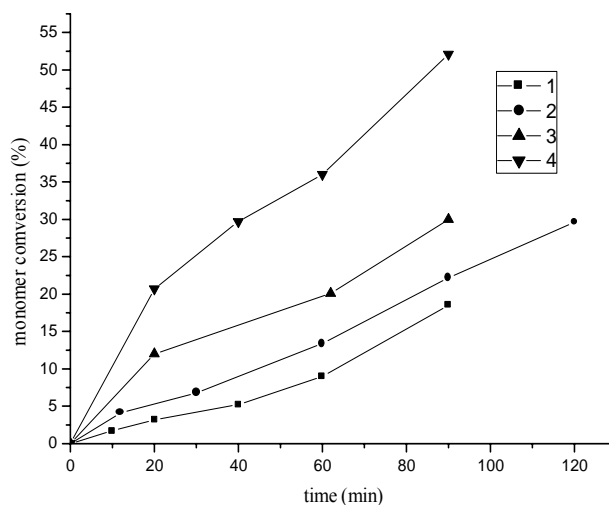
A blue opalescence was observed after 5 min in the presence of  $\beta$ -CD, when the initiator was added, whereas if without  $\beta$ -CD, a blue opalescence appear after about 8 min. Increase the concentration of  $\beta$ -CD induced accelerating the reaction, the reaction system was turned to be forbid faster.

From **Figure 1**, it can be found that the average particle sizes increased slightly with the increase of  $\beta$ -CD concentration. The particle-size distribution narrowed (**Figure 1 b, c, d**) than that without  $\beta$ -CD (**Figure 1 a**). The particle-size distribution narrowed with the increase of  $\beta$ -CD content.

The polymerization rate of the polystyrene latexes was proportional to the amount of

$\beta$ -CD (shown in **Figure 2**). The final conversions were also increased with increase  $\beta$ -CD concentration (shown in **Table 1**). The effect of  $\beta$ -CD to accelerate the polymerization and shorten the reacting time is desired.

**Figure 2** Monomer conversion as a function of time in the presence of different amounts of  $\beta$ -CD (1. 0 g, 2. 0.25 g, 3. 0.5 g, 4. 1.0 g)



The above observations strongly suggested that the main role of  $\beta$ -CD in these polymerizations is to aid the transport of monomer to the loci of polymerization. The increase of the amount of CD will increase the rate of propagation of styrene to the locus of polymerization. Because  $\beta$ -CD can shorten the time of nuclei period, so the particle-size distribution was also narrowed. But the particle size was increased with the increase of concentration of CD. It seems that CD in these systems does not play a major role in the colloidal stability. S. Rimmer<sup>5</sup> used dodecyl methacrylate as monomer was also observed the similar phenomena. But recently, S. Joachim<sup>6</sup> found that the average particle sizes decreased with increasing CD concentration when the monomer was added in a semicontinuous way. Thus the real role of CD in the polymerization, especially in the nuclei period, is not understood completely and is subjected of our further investigations.

### Conclusion

It was shown from above results that  $\beta$ -CD could greatly accelerate the polymerization. The final monomer conversion could be up to 95% in the presence of  $\beta$ -CD within 5 hours. Furthermore, the polymer particles had a narrower particle size distribution. The method we described gives a simple way to the synthesis of polymer particles with narrow PSD without using surfactants or solvent mixtures. The latexes can be used directly without further purification.

**References**

1. H. Ritter, M. Tabatabai, *Progress in Polymer Science*, **2002**, 27,1713.
2. S. Bernhardt, P. Glockner, A. Theis, *Macromolecules*, **2001**, 34,1647.
3. H. Ritter, S.B. Sabine, P. Stein, *Macromolecules*, **2003**, 36,318.
4. C. H. Yan, X. X. Fang, X. W. Li, *Polymeric Materials Science and Engineering*, **1991**, 4, 26.
5. S. Rimmer, P. Tattersall, *Polymer*, **1999**, 40,5729.
6. S. Joachim, V. A. Huub, V.R. Christiaan, *Macromolecules*, **2003**, 36,50.

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