

# Monodisperse, micrometer-sized low molar mass polystyrene particles by two-stage dispersion polymerization

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## Abstract

Free-radical dispersion polymerization of styrene was carried out in ethanol and in ethanol–water mixtures in the absence and presence of carbon tetrabromide (CBr<sub>4</sub>) as a chain transfer agent. When CBr<sub>4</sub> was present at the onset of the reaction, particles with a broad size distribution were obtained. If, however, the addition of CBr<sub>4</sub> was delayed ca 1 h, so that the particle nucleation step was complete, then 1–2 wt% chain transfer agent, dissolved in monomer plus solvent, could be added to the reaction without a deleterious affect on particle formation. The particle size and size distribution was essentially identical to that obtained in the absence of CBr<sub>4</sub>. When more CBr<sub>4</sub> was added, other problems arose. These problems appeared to be due to solubility of low molar mass polymer in the reaction medium. They could be overcome by running the reaction in ethanol–water mixtures (e.g. 5 wt% water) to decrease the solubility of oligo-styrene at 70 °C, the reaction temperature. In this way, monodisperse particles could be prepared in the presence of 3 wt% CBr<sub>4</sub> based upon total styrene, consisting of polymers with  $M_n = 7060$ ,  $M_w/M_n = 2.4$ .

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## 1. Introduction

The properties of polymer particles depend on their size, shape, and surface functionality, as well as the molecular weight and the molecular weight distribution of their constituent polymer molecules. Many applications require particles consisting of relatively low molecular weight polymer. These particles are expected to swell more with small molecules such as perfumes, drugs or biomolecules than particles of high molecular weight polymer and, therefore, may function as a reservoir or carrier for these species. Polymer particles formed from low molecular weight polymer may be of interest from a different perspective. Several research groups have described the preparation of micron-sized polymer particles by an emulsion polymerization procedure in which a swelling step by monomer is an essential feature of forming large particles [1–3]. It is possible that one may achieve enhanced swellability if the seed particles used in these reactions consisted of polymer of low molar mass.

For polymers produced by a free radical reaction, the two strategies to lower the (number-averaged) molecular weight are to use a large amount of initiator, which increases the bimolecular termination reaction, or to add a small amount of a chain transfer agent. The chain transfer agent (CTA) serves the dual role of terminating growing chains and subsequently initiating new chains. The choice of a chain transfer agent in a given reaction depends upon a balance between the transfer rate of the CTA and the propagation rate of the monomer. For optimum chain transfer agents, these two rates are similar, and the chain transfer constant has a value near unity.

While many groups have investigated the use of chain transfer agents in solution polymerization and emulsion polymerization [4–6], there have been fewer studies of chain transfer in dispersion polymerization. We know of only two publications that examined these reagents in any detail, the publication by Paine et al. [7] more than a decade ago, and the recent publication by Ahmad and Tauer [8]. This apparent lack of interest is related to problems in the reaction caused by the introduction of a chain transfer agent. For example, in the dispersion polymerization of styrene in ethanol [9], micron-sized monodisperse particles are obtained when no CTA is present. However, when even small amounts of a chain transfer agent such as carbon tetrabromide (CBr<sub>4</sub>) [8] were added to the reaction, many attractive features of the reaction disappeared. The polymerization rate decreased and the particle size

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distribution broadened considerably. In the presence of 0.36 wt% butanethiol as a chain transfer agent, polydisperse particles were obtained; the GPC chromatograms of these particles contained several broad peaks and the ratio  $M_w/M_n$  was around 100 [7]. Dispersion polymerization reactions are notoriously sensitive to the presence of problematic reactants. For example, attempts to synthesize cross-linked particles in this way have not been very successful [10,11], because the presence of the cross-linking agent in the reaction leads to a broad size distribution or non-spherical particles. Even a small perturbation such as the introduction of a small amount of a polymerizable fluorescent dye had a deleterious effect on the polymerization of styrene in ethanol [12–14].

We recently discovered that many of the problems associated with dispersion copolymerization could be avoided if one delayed addition of the second monomer until the nucleation stage was complete and the particle number in the reaction became constant. We called this methodology ‘two-stage’ dispersion polymerization [15,16]. A recent study by Yasuda et al. [17] demonstrated that the nucleation stage of dispersion polymerization was complete at less than 1% monomer conversion, which for styrene under our reaction conditions (70 °C) corresponds to less than 15 min reaction time. For dispersion copolymerization of styrene in ethanol, we were able to prepare monodisperse PS particles containing a covalently bound fluorescent dye [14], and PS particles cross-linked with ethylene glycol dimethacrylate (EGDMA) or divinylbenzene (DVB) [18], carboxyl-functionalized PS particles [19], by delaying addition of the problematic comonomer after the nucleation stage was over.

The fundamental idea of this approach is that the particle nucleation step is much more sensitive than the particle growth step of the reaction. Deferred monomer addition avoids interference with the nucleation stage. One still has to contend with factors that affect the particle growth stage. For example, in the synthesis of cross-linked particles using divinylbenzene or more than 1 mol% EGDMA, other steps had to be taken in terms of timing the addition of the cross-linking agent to maintain particle swellability during the reaction [18]. In the synthesis of carboxyl-functionalized particles using more than 2 mol% of acrylic acid, improved colloidal stability is required to prevent the coagulation of carboxyl-functionalized particles during the reaction [19].

Here we extend these ideas to the introduction of  $\text{CBr}_4$  as a chain transfer agent into the dispersion polymerization of styrene in ethanol and ethanol–water mixtures. We show that one can obtain particles with a narrow size distribution, but one has to adjust the composition of the medium in such a way that the low molar mass polymer produced in the reaction continues to precipitate from the medium.

## 2. Experimental

### 2.1. Reagents

All organic and polymeric reagents were used without further purification, including styrene (Aldrich), Carbon

tetrabromide ( $\text{CBr}_4$ , Aldrich), methanol, ethanol, polyvinylpyrrolidone (PVP) (Aldrich PVP55,  $M_w = 55,000$  g/mol), 2,2'-azobis(2-methylbutyronitrile) (AMBN, Wako Pure Chemical Industries Ltd), Triton X-305 [20] (70% solution in water, Aldrich). Water was purified through a MilliQ purification system.

### 2.2. One-stage dispersion polymerization

The standard recipe for the one-stage dispersion polymerization of styrene in the presence of  $\text{CBr}_4$  in ethanol is listed in Table 1. The following procedure was used: all the ingredients were added to a 250 mL three-neck reaction flask equipped with a condenser and a gas inlet. After a homogeneous solution formed at room temperature, the solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. Then the flask was placed in a 70 °C oil bath and stirred mechanically at 100 rpm. The monomer conversion was monitored gravimetrically by removing aliquots during the polymerization.

### 2.3. Two-stage dispersion polymerization

The standard recipe for the two-stage dispersion polymerization of styrene in the presence of  $\text{CBr}_4$  in ethanol is also listed in Table 1. The following procedure was used: all of the stabilizer (PVP), the co-stabilizer (Triton X-305) and initiator (AMBN), and half of the monomer and ethanol were added to a 250 mL three-neck reaction flask equipped with a condenser and a gas inlet. After a homogeneous solution formed at room temperature, the solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. Then the flask was placed in a 70 °C oil bath and stirred mechanically at 100 rpm. The  $\text{CBr}_4$  was dissolved in the remaining styrene plus ethanol at 70 °C under nitrogen. After the  $\text{CBr}_4$  was dissolved and the polymerization reaction had run for 1 h, the hot  $\text{CBr}_4$  solution in another half of the monomer and ethanol was added into the reaction flask. The monomer conversion was monitored gravimetrically by removing aliquots during the polymerization, but we do not report the data. The reaction was continued for 24 h and the styrene conversion reached 90–95%.

Table 1  
Standard recipe for the dispersion polymerization of styrene with chain transfer agent in ethanol

	Materials	Amount (g)		
		One-stage method	Two-stage method	
			1st stage	2nd stage
Monomer	Styrene	6.25	6.25	6.25
Chain transfer agent	$\text{CBr}_4$	0.063	0	0.25
Medium	Ethanol	18.75	18.75	18.75
Stabilizer	PVP55	1.0	1.0	
Co-stabilizer	Triton X-305	0.35	0.35	
Initiator	AMBN	0.25	0.25	

#### 2.4. Characterization of particle size and size distribution

The particle size was examined by both optical microscopy (Olympus, X41) and scanning electron microscopy (SEM, Hitachi S-5200). To prepare samples for optical microscopy, the final polymer particle suspension was diluted with water, and a drop was placed on a clean glass microscope slide. The particle size and size distributions were examined by SEM. A particle-size histogram was constructed from measurements of 200–300 individual particles from the electron micrographs.

The molecular weights and molecular weight distributions of the constituent polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using polystyrene calibration standards. GPC measurements were performed on a Waters liquid chromatograph equipped with a Waters 480 R410 differential refractometer (RI) detector. The polymer samples for GPC analysis were prepared as follows: The particles were centrifuged at 2000 rpm for 10 min. The precipitated particles were redispersed into fresh ethanol/water (95:5, wt/wt) and centrifuged again. This process was repeated four times. After the particles were dried, they were dissolved in chloroform, and the solution was passed through a 0.45  $\mu\text{m}$  filter before injecting it into the GPC column.

### 3. Results and discussion

Dispersion polymerization is defined as a polymerization in which the monomer and all other reactants are soluble in the reaction medium, but the polymer formed in the reaction is insoluble in the medium. Dispersion polymerization differs from precipitation polymerization in that the presence of a polymeric stabilizer provides colloidal stability to the newly formed insoluble polymer particles and prevents further coagulation. Dispersion polymerization starts as a solution polymerization reaction. The homopolymer chains grow in size until they become insoluble in the reaction medium. The solubility of these polymers is a function of their molecular weight, composition, the reaction temperature, and the composition of the reaction medium. A polymer with a molecular weight larger than a certain critical value ( $M > M_{\text{crit}}$ ) precipitates and aggregates to form colloiddally unstable precursor particles (nuclei). These nuclei coalesce and adsorb stabilizers from the medium onto their surface until they become colloiddally stable. At this point, particle nucleation ceases. Once the total number of particles in the system is fixed, the nucleation stage of the reaction is over. Polymers formed in subsequent polymerization of monomer in solution should precipitate and be captured by the existing particles.

The addition of chain transfer agents decreases the molecular weight of the formed polymer and may increase the solubility of the polymer. The solubility and the critical molecular weight of the formed polymers are very critical for the particle nucleation, because the nucleation stage determines the resultant particle size and size distribution. The solubility and the critical molecular weight of the polymers formed are also very important for the particle growing stage because they

determine whether the formed polymers can be captured by the existing particles.

$\text{CBr}_4$  is an efficient chain transfer agent for radical polymerization of styrene due to a suitable transfer constant ( $C_{\text{tr}}=1.8$ ) [21]. In this work,  $\text{CBr}_4$  was used in free radical dispersion polymerization of styrene in ethanol and in ethanol–water mixtures to decrease the molecular weight of formed polystyrene (PS).

#### 3.1. Low $\text{CBr}_4$ content: one-stage vs. two-stage process

In this section, we examine dispersion polymerization of styrene with 1 wt% of  $\text{CBr}_4$ . Two different processes, the traditional one-stage method and the two-stage method, were compared in this work. First we examined traditional dispersion polymerization in which all ingredients including 1 wt% of  $\text{CBr}_4$  were present at the beginning of the reaction. Fig. 1(A) and (B) shows the SEM images of PS particles prepared following the recipe given in Table 1 (a summary of all of the samples prepared and their characteristics is presented below in Table 2). In the absence of  $\text{CBr}_4$ , the resulting particles were spherical with a diameter of 2.0  $\mu\text{m}$  and a very narrow size distribution (sample SO-0, Fig. 1(A)). In an essentially identical reaction run in the presence of 1 wt% of  $\text{CBr}_4$ , the average diameter of the resulting PS particles increased to 2.9  $\mu\text{m}$ , and the particle size distribution became much broader (1–7  $\mu\text{m}$ , sample SO-1, Fig. 1(B)).

Our results are very similar to those of Ahmad and Tauer [8], who recently reported their experiments on this system. Polydisperse PS particles were obtained even with only 0.5 wt% of  $\text{CBr}_4$ . They also reported a significant retardation in the polymerization rate at higher  $\text{CBr}_4$  content. This result is in contrast to that found for a homogeneous bulk or solution free radical polymerization of styrene [22], in which the presence of  $\text{CBr}_4$  does not affect the overall rate of polymerization. Ahmad and Tauer attributed the rate retardation they observed to frequent exit and reentry of oligostyrene radicals to terminate radicals already growing within the particles.

We found that when 1 wt% of  $\text{CBr}_4$  was present at the beginning of the dispersion polymerization reaction, the nucleation stage, as inferred from the onset of turbidity, became much longer, increasing from less than 10 min without  $\text{CBr}_4$  to more than 1 h in the presence of 1 wt% of  $\text{CBr}_4$ . The turbidity onset time became longer with an increase of  $\text{CBr}_4$  content. This lengthened nucleation stage caused by the presence of  $\text{CBr}_4$  affected not only the particle size and particle size distribution, but also the kinetics of polymerization. It is well known that particle phase (bulk) polymerization is much faster than solution phase polymerization. We think that the retardation of the polymerization rate may be due to a lengthened nucleation stage accompanied by solution polymerization.

We recently developed a novel strategy for carrying out dispersion polymerization reactions in which problematic ingredients that lead to particle polydispersity are added to the reaction only after the nucleation stage is complete. We

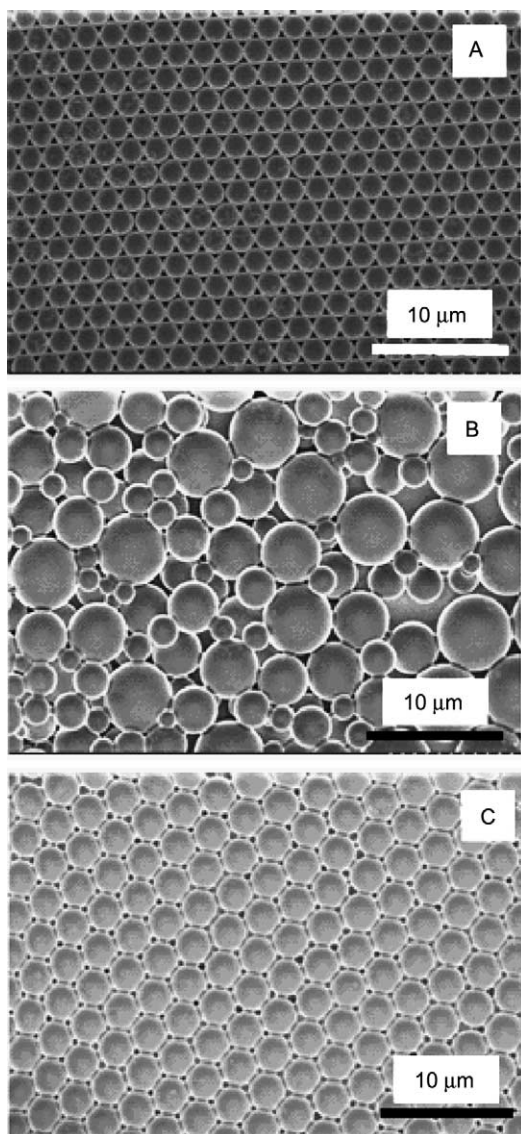


Fig. 1. SEM images of PS particles prepared in ethanol by different processes according to Table 1. (A) one-stage method without  $\text{CBr}_4$  (sample SO-0, Table 2), (B) one-stage method with 1 wt%  $\text{CBr}_4$  (sample SO-1), (C) two-stage method with 1 wt%  $\text{CBr}_4$  (sample ST-1).

Table 2  
Effect of chain transfer agent on the molecular weight, molecular weight distribution, the particle size and size distribution

Sample	$\text{CBr}_4$ (wt%)	$D$ ( $\mu\text{m}$ )	CV (%)	$\bar{M}_n$	PDI	Method	Medium	Remark
SO-0	0	2.0	< 1	–	–	One-stage	Ethanol	Monodisperse
SO-1	1	1–7	–	9220	2.59	One-stage	Ethanol	Polydisperse
ST-01	0	3.0	< 1	21,160	3.65	Two-stage	Ethanol	Monodisperse
ST-02	0	3.0	< 2	–	–	Two-stage	Ethanol/water	Monodisperse
ST-1	1	2.9	< 1	12,890	2.82	Two-stage	Ethanol	Monodisperse
ST-2	2	3.1	15	–	–	Two-stage	Ethanol	Uniform
ST-3	3	3.3	30	6610	2.12	Two-stage	Ethanol	Polydisperse
ST-4 <sup>a</sup>	3	1–4	> 50	–	–	Two-stage	Ethanol/water	Polydisperse
ST-5 <sup>b</sup>	3	3.1	< 1	7050	2.42	Two-stage	Ethanol/water	Monodisperse
ST-6 <sup>c</sup>	3	2.9	< 1	7060	2.42	Two-stage	Ethanol/water	Monodisperse

$$\text{CV} = (1/m) \sum_{i=1}^n (|D_i - D_{\text{av}}|/D_{\text{av}}), D_{\text{av}}: \text{the average diameter of all particles}$$

<sup>a</sup> Five weight percent water (based on the total ethanol and water) in ethanol was added by batch.

<sup>b</sup> Five weight percent water (based on the total ethanol and water) in ethanol was added over 4 h.

<sup>c</sup> Ethanol/water (95:5, wt/wt) was used as the initial reaction medium.  $\text{CBr}_4$  mixed with styrene and ethanol/water (95:5, wt/wt) was added batch-wise 1 h after the start of the polymerization.

refer to this strategy as a ‘two-stage’ dispersion polymerization reaction. There is evidence in the literature [17] that the nucleation stage is complete at a very low monomer conversion, typically a few percent. Thus one can add these reagents, dissolved in monomer plus additional solvent, at a low monomer conversion and still maintain the attractive features of dispersion polymerization.

In the experiments described here,  $\text{CBr}_4$ , dissolved in half of the monomer plus half of the total solvent, was added typically one hour after the first stage of the reaction had begun. Except where noted, the amount of the chain transfer agent added in all experiments described here is based on total styrene. For example, when 1 wt% of  $\text{CBr}_4$  mixed with styrene and ethanol was added 1 h after the start of polymerization, monodisperse PS particles with an average diameter of 2.9  $\mu\text{m}$  were obtained (sample ST-1, Fig. 1(C)). These particles have a similar particle size and size distribution to those prepared by the two-stage method without any  $\text{CBr}_4$  (sample ST-01, Table 2). There is some suggestion in the SEM image of these particles that slight particle deformation occurred as the particles came into contact during drying, perhaps due to the lower molecular weight. These monodisperse PS particles were easily redispersed in water or in ethanol without any coagulum. By gel permeation chromatography (GPC), this sample ST-1 was characterized by  $M_n = 12,900$ ,  $M_w/M_n = 2.82$ . Tests of the reaction indicated that monodisperse seed particles were formed in situ in less than 15 min in the reaction without any  $\text{CBr}_4$  present. We infer that polymerization that occurred after the  $\text{CBr}_4$  was added to the system generated polymer that was formed either inside existing particles, or was formed in solution and precipitated onto existing particles. No detectable secondary nucleation took place.

### 3.2. The effect of increased amounts of $\text{CBr}_4$ added in the two-stage method

In this section, we see that the reaction outcome becomes considerably more complex when larger amounts of  $\text{CBr}_4$  are employed in the reaction. A number of factors become

important. These include the composition of the reaction medium and the details of delayed addition of  $\text{CBr}_4$  to the reaction.

In the experiments described above, ethanol was used as the solvent. When larger amounts of  $\text{CBr}_4$  were added 1 h after the beginning of the reaction, monodisperse particles no longer formed. For example, when 2 wt% of  $\text{CBr}_4$  (based on total styrene), mixed with styrene and ethanol was added 1 h after the beginning of the reaction, the resulting PS particles were relatively uniform but a significant fraction of larger particles were formed (sample ST-2, Fig. 2(A)). When 3 wt% of  $\text{CBr}_4$  was added in the second stage, many bigger particles were formed, and the system was no longer characterized by a narrow size distribution of particles (sample ST-3, Fig. 2(B)).

GPC spectra of PS the isolated polymer (Fig. 3) show the effects of the chain transfer agent,  $\text{CBr}_4$ , on the polymer molecular weights of PS particles prepared by two-stage dispersion polymerization. As expected, the molecular weights decreased with the increase in  $\text{CBr}_4$  content. The peak of PS seed particles formed in situ during the nucleation stage should appear at a higher molecular weight position, but is not visible in these chromatograms due to the low content of seed particles.

With increased amounts of  $\text{CBr}_4$ , the PS particles became much less monodisperse. We attribute the changes that occur at elevated concentration of chain transfer agent to the formation of a significant fraction of polymer too small to precipitate at the reaction temperature. For a given solvent composition and

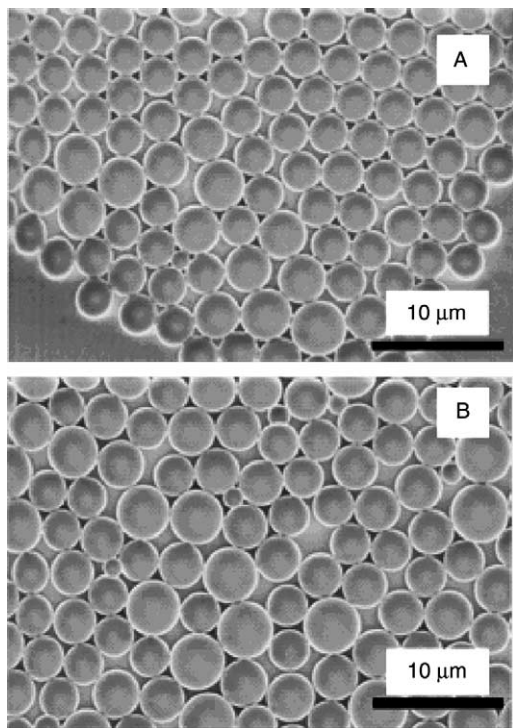


Fig. 2. SEM images of PS particles prepared in ethanol by the two-stage method carried out in the presence of different amounts of  $\text{CBr}_4$  according to Table 1. (A)  $\text{CBr}_4$  2 wt%, (B)  $\text{CBr}_4$  3 wt%.

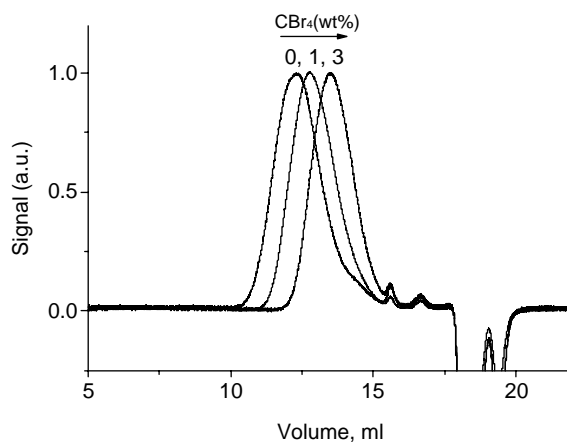


Fig. 3. GPC chromatograms of PS particles prepared by the two-stage method carried out in the presence of different amounts of  $\text{CBr}_4$  with ethanol as the solvent (0, 1, 3 wt%).

temperature, there is a critical molecular weight ( $M_{\text{crit}}$ ) above which the polymer will precipitate. The critical molecular weight for PS in ethanol at 70 °C is ca. 12,000 [17]. The polymer that remains in solution will not be captured by existing particles during the polymerization reaction, but will precipitate onto them or form new particles (with a broad range of sizes) once the reaction mixture is cooled to room temperature. With 1 wt%  $\text{CBr}_4$ ,  $M_n$  is about 13,000, only a fraction of the PS has  $M < M_{\text{crit}}$ . With 3 wt% of  $\text{CBr}_4$ ,  $M_n$  is only about 6600. A larger fraction of the PS has a molecular weight less than 12,000. The  $M_w/M_n$  ratio of PS particles with 3 wt% of  $\text{CBr}_4$  is 2.12, less than the  $M_w/M_n$  ratio of PS particles with 1 wt% of  $\text{CBr}_4$ , 2.82 and also less than the  $M_w/M_n$  ratio of PS particles without  $\text{CBr}_4$ , 3.65.  $M_w/M_n$  is usually much narrower for solution polymerization than for heterogeneous polymerization.

When the  $\text{CBr}_4$  content exceeds a critical point, the PS molecular weight will become too low to precipitate in ethanol at the reaction temperature during the whole process. Thus the reaction will change from dispersion polymerization to solution polymerization, and no particles can be formed. Of course, polymer will precipitate when the reaction is cooled, but the particles formed will have a wide size distribution. One way to obtain particles with low molecular weight in dispersion polymerization of styrene is to use a more polar medium to decrease the value of  $M_{\text{crit}}$ .

One approach is to add water to the reaction medium after the end of the nucleation stage to increase the polarity of the medium. In one experiment, after the polymerization had run for 1 h, 3 wt% of  $\text{CBr}_4$  and 5 wt% of water (based on the total ethanol + water) was mixed with half the ethanol and styrene and added over about 3 min to the reaction. Under these conditions, the resulting PS particles were polydisperse (sample ST-4, Fig. 4(A)). No larger particles were detected by SEM but a significant population of smaller particles was found in the system, presumably due to secondary nucleation. In another reaction, after the polymerization had run for 1 h, 3 wt%  $\text{CBr}_4$  in half of the ethanol plus styrene was added as

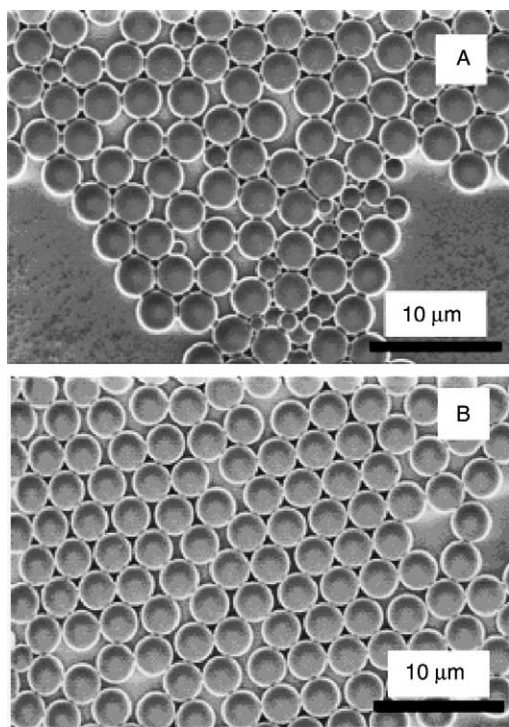


Fig. 4. SEM images of PS particles prepared by the two-stage method with 3 wt%  $\text{CBr}_4$  using different water addition procedures. (A) 5 wt% of water (based on the total ethanol + water) mixed with ethanol was added batch-wise, (B) 5 wt% of water (based on the total ethanol + water) mixed with ethanol was added slowly over 4 h.

described above, and then a mixture of water (2 g, 5 wt% based on the total ethanol + water) and ethanol (8 g) was added slowly over 4 h. Under these circumstances, the resulting particles were monodisperse with no evidence of secondary nucleation (sample ST-5, Fig. 4(B)). Slightly higher molecular weight and broader molecular weight distribution were obtained compared with that in ethanol due to the increase of the particle phase polymerization.

Slower water addition provided the system an opportunity to adjust to the changing circumstances. The PS oligomers generated in the solution phase were captured gradually by the existing particles, and possibly some free PVP-g-PS stabilizer present in solution were gradually adsorbed onto the existing particles before any new particles were nucleated.

Another approach to increase the polarity of the medium is to use the same ethanol–water mixture for both the nucleation and particle growth stages. This approach has the advantage of simplicity and is often effective at preventing the formation of new particles. As a test of this idea, we ran reactions in a mixture of 95 wt% ethanol 5% water. A number of authors have shown that dispersion polymerization of styrene can be run in water–ethanol mixtures. The overall influence of adding a small amount of water to the traditional one-stage dispersion polymerization reaction is to decrease particle size while maintaining the narrow size distribution [7]. This approach provides another strategy to decrease the critical molecular

weight of the growing polymer. We investigated whether this change of reaction medium, incorporated into the two-stage polymerization idea, would maintain the narrow particle size distribution and at the same time permit the use of larger quantities of chain transfer agent.

In the following experiments, we used the same recipe in Table 1 except that the solvent during the nucleation stage was an ethanol–water (95/5, w/w) mixture. We first examined the consequences of adding the same amount of styrene and 95 wt% aqueous ethanol, without any  $\text{CBr}_4$ , 1 h after the start of the reaction. In Fig. 5(A), we show an SEM image of sample ST-02. The resulting particles have a similar particle size ( $D=3.0\ \mu\text{m}$ ) to those prepared in ethanol using the two-stage method. A small fraction of smaller particles were formed, which may be formed by secondary nucleation. One should note that this is not an optimized set of conditions for the preparation of monodisperse particles in an ethanol/water (95/5, w/w) medium.

We then examined the consequences of adding  $\text{CBr}_4$  along with styrene in 95 wt% aqueous ethanol to the reaction 1 h after the start. When 3 wt% of  $\text{CBr}_4$  mixed with styrene and ethanol/water (95/5) was added 1 h after the start of the reaction, highly monodisperse PS particles were obtained (sample ST-6, Fig. 5(B)). Surprisingly, no small particles were generated, probably due to the relative difficulty of secondary nucleation by oligomers. In addition, we note that the particle size remained the same as that of the reaction carried out without  $\text{CBr}_4$ . This result emphasizes that the particle number

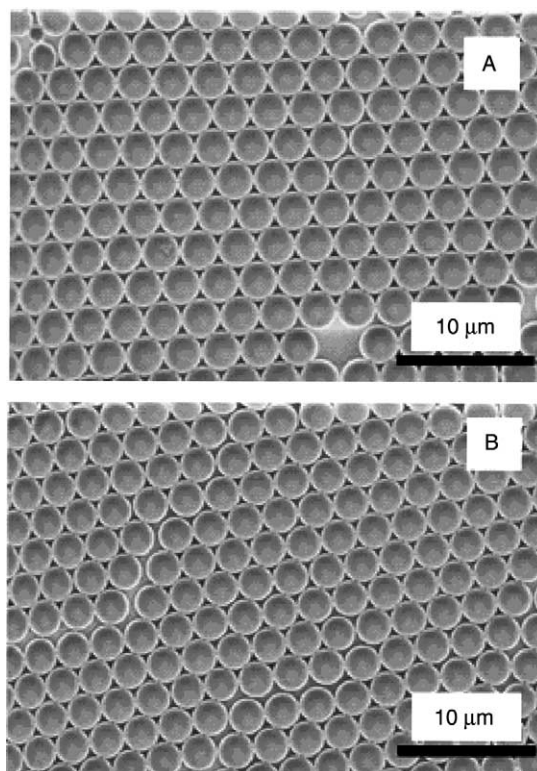


Fig. 5. SEM images of PS particles prepared by the two-stage method using ethanol/water (95/5 wt/wt) as the medium A without  $\text{CBr}_4$ , B with 3 wt%  $\text{CBr}_4$ .

had become constant, and remained constant, during the course of the reaction. These monodisperse particles prepared in the presence of 3 wt% CBr<sub>4</sub> based upon total styrene, consist of polymers with  $M_n=7060$ ,  $M_w/M_n=2.4$ .

#### 4. Summary

Addition of a chain transfer agent such as CBr<sub>4</sub> to the dispersion polymerization of styrene in ethanol leads to a substantial broadening of the particle size distribution and a delay in the onset of particle nucleation. If the addition of CBr<sub>4</sub> is delayed until the nucleation stage is complete, and it is added with a mixture of additional monomer and solvent, one can obtain particles of lower molecular weight, but with the same size and narrow size distribution as when no chain transfer agent is present. Other complications arise if the polymer molecular weight is reduced below the critical value for precipitation from the medium at the reaction temperature. These problems may be overcome by adding small to modest amounts of water to the reaction medium to reduce the critical molecular weight for polymer precipitation.

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