

Formation of Primary Particles in Vinyl Chloride Polymerization

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Synopsis

The formation of primary particles in agitated bulk polymerizations of vinyl chloride was found to proceed in two stages. The first stage occurred at the very beginning of the polymerization; the second stage started as the initially nucleated particles began to agglomerate, and continued up to at least 7% conversion. Upon formation, the primary particles were stable and did not agglomerate until reaching a limiting size, which was found to be lower at higher stirring speeds. The number of particles formed in the first stage was independent of agitation and other polymerization parameters. The rate of particle formation during the second stage was equal to the rate of particle agglomeration. Thus the total number of primary particles formed was determined almost exclusively by the rate of particle agglomeration. Addition of the surfactant Span 20 caused an increase in the total number of primary particles. Also, this addition increased the tendency of the particles to fuse together after agglomeration. These effects can be understood to be a consequence of particle destabilization by the surfactant. When a small amount of a high molecular weight PMMA was dissolved in the monomer, the polymerization behaved quite differently. In this case, the primary particles were prevented from agglomeration, reaching a limiting size independent of stirring speed.

INTRODUCTION

The precipitation of poly(vinyl chloride) (PVC) and the formation of colloidally dispersed, primary particles begins early in the bulk polymerization of vinyl chloride monomer (VCM). Primary particles are formed by the agglomeration of very small particles, sometimes referred to as basic particles.¹ These basic particles have been directly observed in investigations at very low conversion of the VCM.²⁻⁴ Probably, basic particles are formed by the coagulation of a few polymer molecules, which have been formed close together during a polymerization event involving a number of chain transfer reactions to monomer.¹ Since the basic particles have no colloidal stability; they coagulate rapidly to yield particles with an initial diameter of about 80 nm, which are referred to as primary particles in this paper. In a study of quiescent polymerizations, Rance and Zichy¹ found that the primary particles reached a diameter of 90 nm at 0.006% conversion. Furthermore, they found that the primary particles increased in size up to at least 0.1% conversion while remaining constant in number.¹ Thus, findings from that study showed that the first stage of primary particle formation is finished before 0.006% conversion.

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The primary particles are believed to be electrostatically stabilized by negative charges.^{3,5} This stabilizing force is weak, and the particles are therefore susceptible to shear-induced agglomeration. Boisel and Fischer⁶ showed that, in an agitated reactor, agglomeration occurred at a critical conversion, somewhere between 0.05 and 0.2%. The conversion at which agglomeration began was found to be dependent on the agitation speed.^{6,7} Agglomeration leads to the formation of large granules with a size of about 100 μm . Such granules have been observed at rather low conversions.⁷

Zichy⁸ has suggested that the primary particles have a tendency to form closely packed clusters containing 13 particles. These clusters eventually fuse and grow to a size of about 1–2 μm , which is the approximate size of the structural units in the final resin grains often referred to as primary particles.³

The purpose of this paper is to discuss the results from an investigation of the formation of primary particles during the second formation stage, and to study the use of sorbitan esters as a mean of controlling the number of primary particles.

EXPERIMENTAL

Polymerization of about 120 g of VCM was carried out at 59°C with 0.11 g of dilauryl peroxide, dissolved in 1 mL of benzene, as initiator. A 200 mL glass-walled reactor was used. The reactor had an internal diameter of 52 mm and was supplied with an anchor stirrer of 48 mm diameter. The conversion was followed by measuring the thermal power of the process, as described previously.⁷ The polymerizations could be interrupted at any level of conversion by transferring the reactor contents to a cool steel vessel. The remaining monomer could then be removed by extraction with ethanol.⁷

The primary particle size distribution was determined by measuring 80–200 particles from scanning electron micrographs (SEM) taken from 6 to 10 randomly chosen areas of the sample. The particle size distribution was used to calculate the particle concentration and the theoretical specific surface of the sample. The calculations were made assuming all of the polymer was present as spherical particles, consisting of solid PVC with a density of 1400 kg/m^3 .

The samples investigated in the SEM were coated with 150 Å Au/Pd to prevent charging. The thickness of the Au/Pd coating was corrected for in the particle size calculations. The accuracy of this correction was tested by coating monodisperse polystyrene latex particles with a diameter of 0.16 μm with different amounts of Au/Pd. Layers of 100, 300, and 400 Å increased the measured particle diameters by 250, 550, and 900 Å, respectively. In this case, the particle sizes could be determined with an accuracy of ± 100 Å. With the PVC samples the accuracy was lower because of lower micrograph quality. No correction for the possible shrinkage of the PVC particles in the electron beam (25 kV) was made.

Samples for nitrogen BET measurements were dried and degassed in vacuum for a minimum of 24 h at room temperature and then for 2 h at 60°C.

The sedimentation volume of the agglomerated primary particles was determined as a function of conversion by measuring the height of the sediment in the reactor when the agitator was stopped during the polymeriza-

tion. Sedimentation time (period without agitation) was between 60 and 120 s. The agitator was stopped for less than 6% of the total polymerization time.

The nonionic surfactants Span 20 (sorbitan monolaurate), Span 80 (sorbitan mono-oleate), and Tween 21 (tetraoxyethylene sorbitan monolaurate) were used after removal of the VCM insoluble fractions.

RESULTS AND DISCUSSION

Particle Formation Without Additives

During polymerization of VCM without additives, the particles grew rapidly in size at low conversion (Figs. 1 and 2), in agreement with previous results.¹ Eventually a limiting particle size was reached; over the conversion range studied, no particles exceeded that limiting size. At an agitator tip speed of 1.5 m/s, the limiting size was 0.18 μm , reached at a conversion of 0.2% (Fig. 1). At the lower agitation speed of 0.4 m/s, the limiting size of 0.35 μm was reached at a conversion slightly above 1% (Fig. 2).

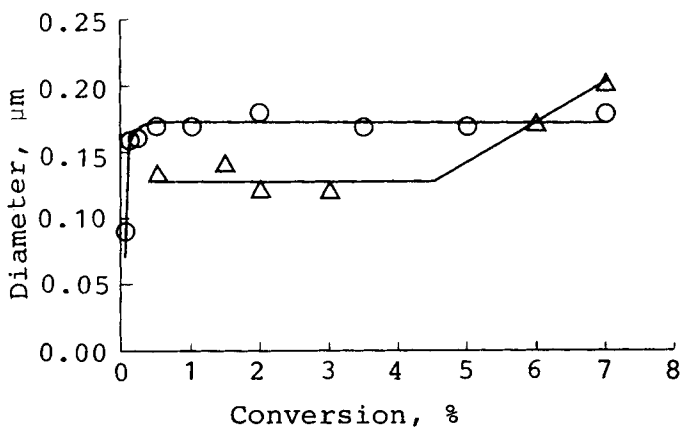


Fig. 1. Primary particle size as determined in experiments with an agitator tip speed of 1.5 m/s, (O) without additives; (Δ) with 0.2% Span 20.

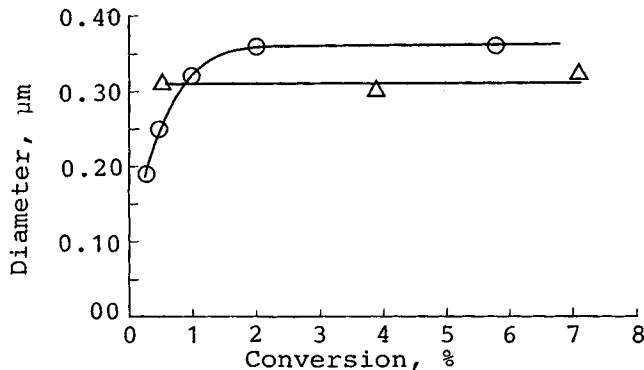


Fig. 2. Primary particle size as determined in experiments with an agitator tip speed of 1.5 m/s, (O) without additives; (Δ) with 0.2% Span 20.

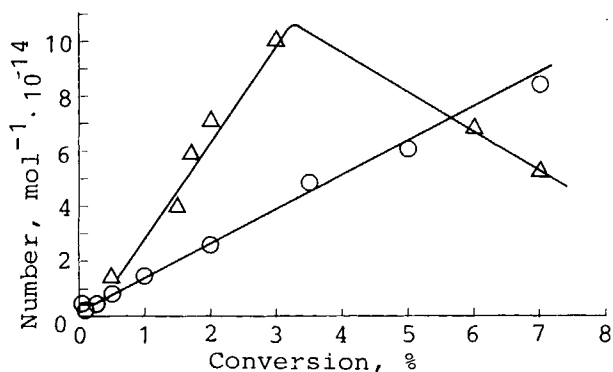


Fig. 3. Number of primary particles/mol of VCM found in experiments at an agitator tip speed of 1.5 m/s, (○) without additives; (Δ) with 0.2% Span 20.

A calculation of the number concentration of particles revealed that, when the particles had reached their limiting size, their total number started to increase (Figs. 3 and 4). Thus, a second stage of primary particle formation occurred. The particle concentrations in Figures 3 and 4 refer to the total number of particles, that is, the sum of free primary particles and primary particles in the agglomerates.

The initial period, during which the particle number was constant, was relatively long at the lower agitation speed (Fig. 4). The number of particles present during this period was found to be equal to the number of particles formed in the first formation stage. Close inspection of Figure 3 shows that the particle number curve also has an intercept at the higher stirring speed. This intercept has about the same value as the intercept in Figure 4. The experimental values show that the number of particles formed in the first formation stage ($\times 10^{13} \text{ mol}^{-1}$) is between 1.2 and 4.5. These results are similar to results from a number of other studies, which showed the number of particles at the beginning of the polymerization to be as follows: ($\times 10^{13} \text{ mol}^{-1}$) 4.0,² 4.0,⁶ 3.2,¹¹ and 2.0.¹² The agreement between these studies indicates that the first particle formation stage is controlled by the inherent properties of the system, rather than by the reaction conditions or by the

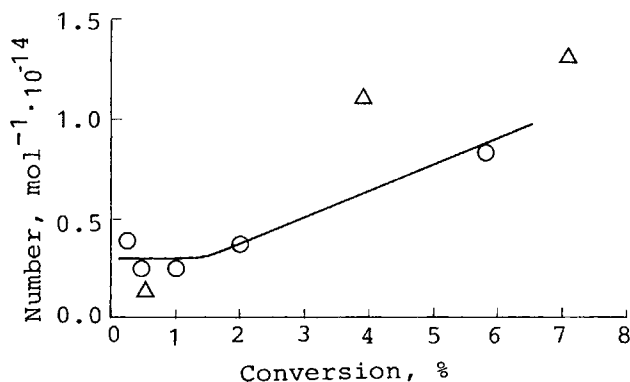


Fig. 4. Number of primary particles/mol of VCM found in experiments at an agitator tip speed of 0.4 m/s, (○) without additives; (Δ) with 0.2% Span 20.

occasional presence of impurities. Therefore, results from this and previous studies show that the number of particles formed in the first stage can only be changed by considerably decreasing the rate of polymerization.⁶

Second Formation Stage

The limiting particle size and the total particle number at a given conversion was found to be strongly influenced by the stirring speed (compare Figs. 1 and 3 with Figs. 2 and 4). As the figures demonstrate, an increase in stirring speed gave particles with a smaller limiting size and resulted in an earlier start and a higher rate of particle formation in the second formation stage. As a previous study reveals, an increase in stirring speed will lead to an earlier start of primary particle agglomeration.⁷ Clearly, the different effects produced by changing the intensity of agitation are closely related, and are most probably caused by the increase of the particle's shear sensitivity with particle size. Such a decrease in stability with growth means that, at low stirring speeds, the particles may grow for a longer period and reach a larger size before they become sufficiently unstable to agglomerate. The high shear field developed at a high stirring speed would cause the particles to agglomerate even after a short growing time and, consequently, at a correspondingly smaller size.

Assuming that the primary particles present during the initial period of polymerization are formed at very low conversions, it is possible to understand that particle agglomeration will induce the formation of new primary particles. The primary particles formed in the first formation stage grow by sweeping up basic particles from the monomer phase. Obviously, if the number of primary particles are constant, they must be picking up all the basic particles formed. By this growth process, the primary particles increase in surface area and in their capacity to sweep up new polymer molecules and basic particles from the monomer phase. This stable situation will be disturbed if the primary particles agglomerate. Agglomeration results in an uneven particle distribution over the monomer phase and in the occurrence of volume elements with a low particle concentration. At a certain level of agglomeration, these volume elements become large enough to permit coagulation of basic particles so that new primary particles can be formed. This mechanism is supported by the finding of Boisel and Fischer,⁶ who observed that small primary particles appeared after the initially formed primary particles had agglomerated.

From this description of agglomeration, it follows that the second stage of particle formation is determined by the rate of agglomeration. Since the number of particles formed in the second formation stage far exceeds the number of particles formed in the first formation stage, it is clear that the total number of primary particles formed in a polymerization process can be varied only by changing the rate of agglomeration. One way of varying the agglomeration rate is by changing the stirring speed; a second is by manipulating the colloidal stability of the primary particles (see below).

Agglomeration and Free Particle Concentration

It has been found that agglomeration of the primary particles by stirring yielded loosely packed grains with a diameter of about 100 μm .⁷ At the highest

stirring speed used in this and previous work, 1.5 m/s, agglomerates of 100 μm diameter were observed at conversions below 1%. Upon stopping the stirrer, these agglomerates sedimented rapidly, forming a sharp boundary between the sediment and an upper, slightly turbid monomer phase, which contained unagglomerated primary particles. This sedimentation shows that grains of an appreciable size were formed very early during polymerization and that small aggregates were absent or very few in number. In an experiment at the high stirring speed, the upper monomer phase obtained after sedimentation of the agglomerates was withdrawn and analyzed. It contained 0.14% PVC in the form of primary particles with an average size of 0.16 μm , in comparison with the overall average particle size of 0.18 μm . These results indicate that the number of unagglomerated particles was $2.3 \times 10^{13} \text{ mol}^{-1}$, a figure in agreement with the number of primary particles formed in the first formation stage. This concentration of unagglomerated particles, at 1% conversion suggests that the concentration of free, unagglomerated particles remains constant during the polymerization process. Hence the rate of particle formation during the second nucleation stage is equal to the rate of agglomeration. The results from these experiments also support the view that the second formation stage begins due to primary particle agglomeration.

Figure 5 gives the sedimentation volume of the agglomerated particles as a percentage of the total volume. The sedimentation volume results are from experiments made at the high stirring speed. The sediment volume is slightly lower than 40% at 1% conversion and asymptotically approaches 100% at about 7% conversion. Within the conversion interval from 1 to 7% conversion, the grain size was found to be about constant at 100 μm . This means that the rapid increase in the sediment volume observed between 1 and 5% conversion (Fig. 5) must be due to the formation of new grains. This conclusion is not in agreement with results reported by Barclay,¹³ which indicated that new grains are not formed above 1% conversion.

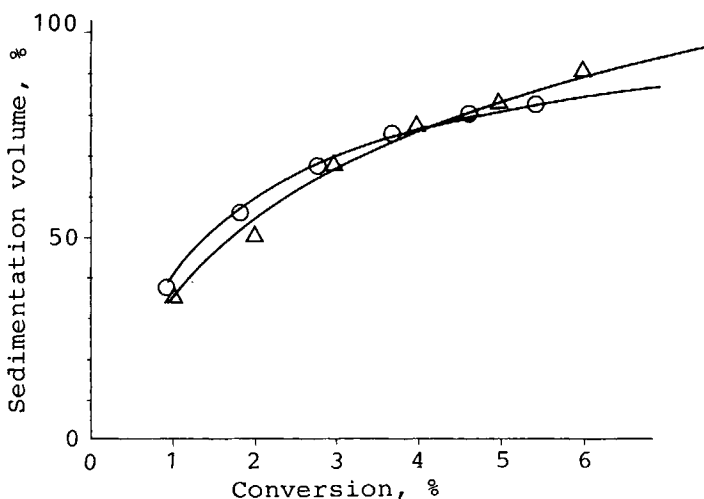


Fig. 5. Sedimentation volume of agglomerates as determined in experiments (O) without additives; (Δ) with 1% Span 20, at an agitator tip speed of 1.5 m/s.

Limiting Particle Size

As discussed in the previous section, the primary particles were found to grow until they eventually became unstable and formed agglomerates. This agglomeration occurred as the particles reached a certain limiting size, which was smaller at the high stirring speed (Fig. 1). The particle size data at conversions beyond the bends in the particle size curves in Figures 1 and 2 refer mainly to agglomerated particles. Thus, these results imply that particle growth appeared to stop, as the primary particles agglomerated and formed porous grains of about 100 μm in size.

Why the agglomerated particles did not grow, or grew at a much lower rate than the free unagglomerated particles, can be explained in several ways;

First, agglomerates move at a lower speed than unagglomerated particles. A particle in an agglomerate thus passes through a smaller liquid volume than a free particle, resulting in a lower absorption rate of polymer from the monomer phase.

Second, in the agglomerate, the individual particles compete with each other in attracting basic particles from the surrounding liquid phase.

Third, basic particles formed in the proximity of agglomerated particles tend to coagulate in the contact zones between particles, thus maximizing the gain in surface free energy. Deposition of polymer in this way was not recorded as particle growth in the SEM micrographs, as the particle diameter was measured in a direction where the particles made no contact with other particles.

Finally, as the total number of particles increases with conversion, the growth rate of the individual particles should decrease with conversion, making it increasingly difficult to detect particle growth.

The importance of the second explanation of the nongrowth behavior of the agglomerated particles can be understood by a simple calculation. The particles grow by two mechanisms: (1) by absorption of polymer (basic particles) from the monomer phase; and (2) by polymerization inside the particles. Because of the gel effect, the specific rate of polymerization inside the particles is about 15 times faster than that in the liquid phase.¹⁸ If the concentration of unagglomerated primary particles is $3 \times 10^{13} \text{ mol}^{-1}$, the average distance between neighboring particles will be 1.5 μm . Therefore, a free primary particle is capable of collecting basic particles formed within a distance of 0.75 μm . Assuming that agglomerated particles also grow by absorbing basic particles formed within a distance of 0.75 μm , the calculation of the relative growth rate of free particles and particles in agglomerates of different geometries is possible. Such calculations showed that the rate ratio of volume growth for free particles; particles in a row; and very densely packed agglomerates where the growth is dominated by gel phase polymerization, would be 39 : 5 : 1. The packing density in a real agglomerate would, of course, be lower than in a densely packed agglomerate, but higher than in a linear row of particles.

The importance of coagulation in the contact zones between agglomerated particles, covered in the third explanation of the limited growth rate of agglomerated particles, was previously demonstrated by comparing the theoretically calculated specific surface of the PVC particles with that determined experimentally by BET (Fig. 6).⁷

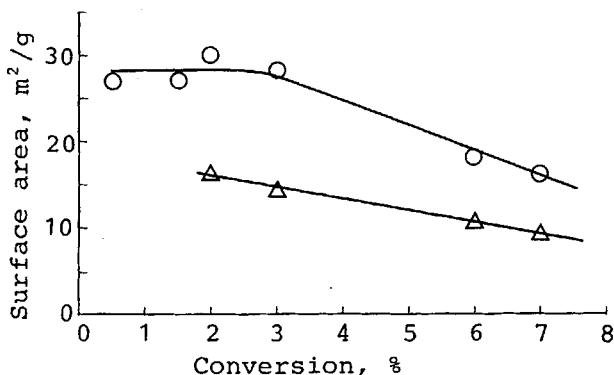


Fig. 6. Specific surface of the polymer obtained in experiments at an agitator tip speed of 1.5 m/s, and in the presence of 0.2% Span 20, (O) calculated specific surface; (Δ) BET.

In addition to the explanations considered here, it is possible that there are further reasons why growth of unagglomerated particles is favored over the growth of agglomerated particles. For example, if a sizeable fraction of the basic particles were charged, they would tend to coagulate with unagglomerated primary particles rather than with agglomerated particles, which have an overlap of the repulsive electrostatic fields.

Particle Stability

The size and number of primary particles formed is determined by the colloidal stability of the particles. It was thus of interest to study if the stability of the particles was affected by the presence of initiator residues at the particle surface or when polymer tacticity is changed. The polymer tacticity affects the solution properties of the polymer in its monomer.¹⁹ If the particle stability were due to steric stabilization by atactic chain segments protruding out from the particle surface into the monomer phase, the polymer tacticity might affect the particle stability.

To study these effects, bulk polymerizations were carried out with azo-bis-isobutyronitrile and dicetyl peroxy dicarbonate as initiators, in addition to dilauryl peroxide. Experiments were carried out at temperatures between 40 and 60°C using initiator concentrations which gave the same polymerization rate in all experiments. The stirring speed was 1.5 m/s and the particle size was determined on samples taken out at 1% conversion. Differences in primary particle size were not observed in these experiments. Thus it was concluded that, initiator fragments or polymer tacticity have little or no effect on the colloidal stability of the primary particles.

The main reason for particle stability therefore would appear to be electrostatic stabilization, caused by the presence of negative charges on the particles.^{1,3,5}

Previous work suggests that the negative charges on the particles are due to chlorine ions, which originate from hydrochloric acid formed by reaction between vinyl radicals and oxygen. Since the oxygen concentration would be very low even after a short time of polymerization, chlorine ions from this source could not stabilize particles formed at higher conversions. As seen in

this investigation, during the second formation stage the particles grew to the same size as those nucleated initially. This means that the particles obtained in the second formation stage would be equally stable as those obtained in the first formation stage. Hence, it is logical to assume that the polymerization process causes the charges to be formed continuously. One possible source of HCl could be radical transfer to polymer. Hydrogen abstraction by chlorine radicals occurs with a frequency of 1-3 events per 10,000 monomer units polymerized.¹⁷

Influence of Span 20

The presence of Span 20 during polymerization was found to give smaller primary particles (Figs. 1 and 2) in a correspondingly higher number (Figs. 3 and 4). It follows from the previous discussion that Span 20 must reduce the colloidal stability of the particles. The mechanism by which this occurs is not understood. Furthermore, it should be noted that this conclusion conflicts with the previous assumption that Span 20 increases particle stability.^{9,10,12}

The specific surface area of the polymer phase decreased rapidly with conversion for the polymer prepared in the presence of Span 20 (Fig. 6). The specific surface reduction of polymers prepared in the presence of Span 20 was much larger than for polymers without additives.⁷ Therefore, particle fusion occurred much more rapidly when Span 20 was present during the polymerization. It is also possible that the more rapid particle fusion in the presence of Span 20 resulted from a reduction in particle stability. A more rapid fusion would be expected if the agglomerates were more densely packed, that is, in a way which gave an increased number of particle-particle contacts. The reasons for particle fusion are as yet slightly unclear. Particle fusion could be due exclusively to precipitation of polymer in the contact zones between the particles. However, fusion could also result if the coagulated particles are forced closer together.

A difference in the packing density or porosity of the grains formed in the presence of Span 20 was not observed in the sedimentation volume measurements (Fig. 5).

The relatively rapid particle fusion observed in the presence of Span 20 may lead to an overestimate of the particle number as calculated from particle size data. If the particle fusion observed were due to precipitation of polymer in the contact zones, and if each particle had four contact zones, then a decrease in the specific surface area of 50% would yield an estimate of the particle number too high by 30%. Although not insignificant, this error is still too small to invalidate the conclusion that addition of Span 20 leads to an increase in the total number of primary particles.

In polymerization experiments carried out in the presence of 0.2% Span 20, 6.8×10^{14} particles/mol were found at 2% conversion. In comparison, 2.7×10^{14} particles/mol VCM were found at 2% conversion in the additive-free polymerization. An increase in the concentration of Span 20 above 0.2% produced no further increase in particle number (Fig. 7).

When polymerization was carried out at high stirring speeds and in the presence of Span 20, an increase in the average particle size was observed at conversions above 3% (Fig. 1). As the particle size distribution seen in Figure 8

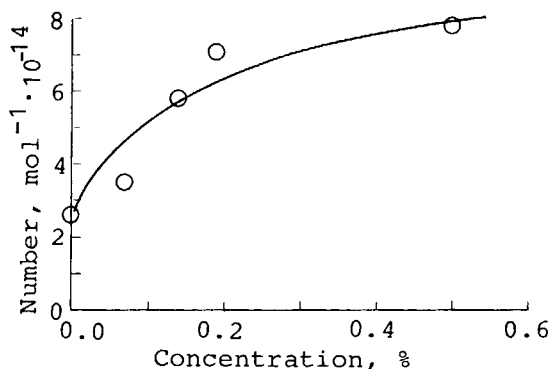


Fig. 7. Number of primary particles per mol of VCM at 2% conversion on addition of Span 20.

shows, this increase was due to the formation of a fraction of large particles with diameters of about 0.3 and 0.4 μm . Clearly these large particles were formed by fusion of smaller particles, since the total particle number decreased at conversions beyond 3% (Fig. 3). Possibly, the large particles were formed by fusion of particle clusters composed of 13 primary particles as discussed by Zichy.⁸ Such 13-member clusters of 0.12 μm particles would have a size between 0.29 and 0.36 μm , depending on whether the space between the agglomerated particles were filled with new polymer or if the particles disappeared by coalescence. The distribution in Figure 8 shows that most of the large particles had a size within these boundaries. This type of fusion process, giving rather large particles, presumably was also occurring when the polymerization was carried out in the absence of additives, but at conversions above 7%.

The effect of other sorbitan esters has also been tested (Table I). Tween 21 and Span 80 were found to affect the particle-limiting size in a way similar to that of Span 20, but to a lesser degree.

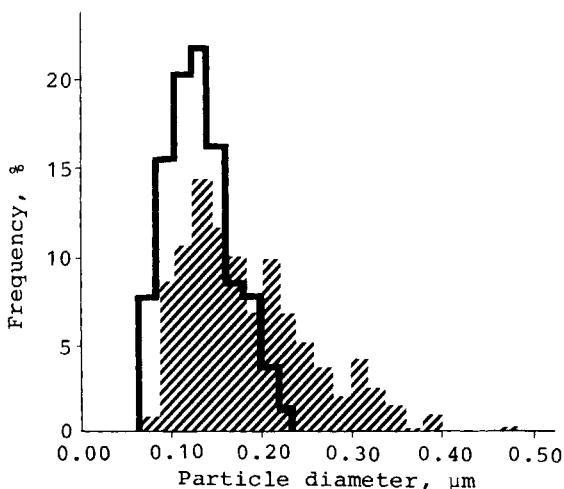


Fig. 8. Primary particle size distribution as determined at 2 and 7% (shaded) conversion. Agitator tip speed 1.5 m/s.

TABLE I
Average primary particle size (d) as determined at 2% conversion in bulk polymerization experiments with and without additives

Additive	Conc. (%)	d (μm)
None	—	0.18
Span 20	0.14	0.13
Span 80	0.14	0.16
Tween 21	0.13	0.16

Influence of PMMA

It has been reported that the addition of PMMA with a high molecular weight gives primary particles with increased resistance to agglomeration.⁷ At a concentration of 0.2% PMMA, the particles remained colloiddally stable up to about 2% conversion at an agitator tip speed of 1.5 m/s. According to the mechanism described above, these conditions should yield very large particles and no secondary particle formation at conversions below 2%, but this was not the case. In the presence of PMMA, the particles reached a limiting size of 0.19 μm at an agitator tip speed of 1.5 m/s (Fig. 9). However, at the lower agitator tip speed (0.4 m/s) and at 1% conversion, the particles had a diameter of 0.21 μm ; hence, they were considerably smaller than those obtained under similar conditions, but in the absence of PMMA. Thus, when PMMA is present, the mechanism of primary particle formation must be completely different from that in absence of PMMA. Possibly, particle nucleation in the presence of PMMA is controlled by grafting of PVC to the PMMA molecules and PMMA acts as a steric stabilizer.

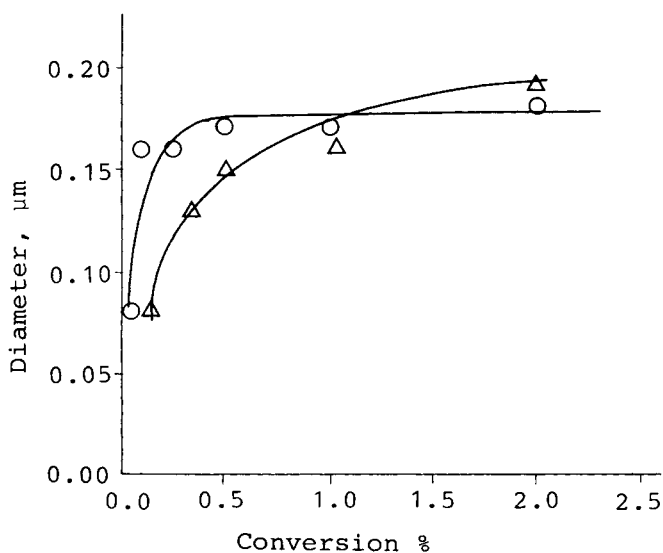


Fig. 9. Primary particle size, as obtained (Δ) with and (O) without the presence of 0.2% high molecular weight PMMA. Agitation 1.5 m/s.

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