

Kinetics of (co)polymerization at the surface of inorganic submicron particles in emulsion-like systems

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KINETICS OF (CO)POLYMERIZATIONS AT THE SURFACE OF INORGANIC
SUBMICRON PARTICLES IN EMULSION-LIKE SYSTEMS

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Abstract: Hydrophilic TiO_2 particles were modified with two different titanates and thus made hydrophobic. "Emulsion" polymerizations were carried out in aqueous dispersions of these particles, stabilized with an anionic surfactant. Polymerization kinetics were determined using a densitometer. The effect of several parameters, like surface modification, surfactant and initiator concentration, and stirring speed on polymerizations were studied. Depending on reaction conditions two competitive polymerizations can take place: one in which polymer is formed at the particle surface and one in which free polymer particles are formed. The TiO_2 was modified with a titanate containing a methacrylic acid ester, which was used as a comonomer. Thus a chemical bond between TiO_2 particles and polymer was obtained. These polymer encapsulated inorganic particles may offer interesting perspectives in those cases, where a good coupling between particles and matrix is important, for instance in latex paints and in polymer composites.

INTRODUCTION

By means of emulsion polymerization processes several types of particles with a core-shell morphology can be obtained. We have used an emulsion polymerization-like technique to obtain particles with an inorganic core and a polymer shell. In this paper we describe on-line conversion measurements for these polymerizations, and a qualitative model to explain the observed effects. The surface of TiO_2 particles is hydrophilic (Ref. 1) and contains several acidic OH groups, which can react with titanate coupling agents. These organic compounds consist of a central titanium atom, one or two small hydrolysable groups (like

isopropyl groups) and two or three long hydrophobic chains or functional groups. A reaction can take place in which an alcohol is formed, leaving the titanate coupled to the pigment surface (Ref. 2). The modified, now hydrophobic, particles are dispersed in an aqueous solution of an anionic surfactant, like SDS^{a)} Part of the surfactant is adsorbed at the particle surface, forming a micelle-like structure in which an "emulsion polymerization" can be carried out. By using a titanate containing a copolymerizable group the modified TiO₂ can be used as a comonomer for polymerization, and a chemical bond between polymer and particle can be obtained. Polymerization kinetics can be studied on line using a densitometer based on oscillatory frequency.

The encapsulated inorganic particles may offer perspectives as pigments in latex paints, where they provide a better coupling between pigment and binder (preventing agglomeration of the pigment, thus improving film properties and gloss), but also as fillers for polymer composites, in flame retardants and as carriers for catalysts.

EXPERIMENTAL

The experiments were carried out with pure rutile (Kronos, RLK). This material was washed with distilled water, in order to remove some K₂SO₄, adsorbed at the surface, and dried under vacuum at 130°C before use. Titanate coupling agents KR7 (diisopropyl isostearoyl methacryloyl titanate) and KRTTS (diisopropyl diisostearoyl titanate) of Kenrich Petrochemicals Inc. were used without further purification. Modification of TiO₂ was carried out in dichloromethane (Merck p.a.): 30 g TiO₂ and 30 g glass pearls were added to the flask containing the titanate dissolved in CH₂Cl₂ in a concentration of about 2 g/l. It is possible to use a mixture of both titanates, but first adding KR7 and afterwards KRTTS proved to be more effective. The total amount of titanates applied always was 1,0 wt% of the TiO₂. The reaction mixture was shaken vigorously for about two hours. Then the glass pearls were removed by filtration and the modified TiO₂ was isolated by centrifugation. The product was washed three times with solvent, and dried at room temperature. Stability of the titanates at the particle surface against solvolysis was studied by means of conductometry (using a radiometer CDM 80 conductivity meter).

a) sodium dodecylsulfate

Polymerizations were carried out with methyl methacrylate (Merck p.a.) distilled at reduced pressure under nitrogen to remove the inhibitor, and a radical initiator based on 4,4'-azobis(4-cyanovaleric acid) (ACPA) (Fluka A.G., purum). Because of its limited solubility in water we decided to use the sodium salt instead of the acid (prepared by reacting the acid with two equivalents of sodium methanolate in methanol). Dispersions of modified TiO_2 in an aqueous solution of sodium dodecylsulfate (SDS, Fluka Chemie A.G., puriss) were made with an Ystral type X1020 high shear stirrer. A small amount of 2-propanol (Merck, p.a.) was added to prevent foaming, and also as an internal standard for monomer conversion measurements by means of gas chromatography. The mixture was added to a 1 liter double-walled thermostated reaction vessel, and flushed with nitrogen in order to remove oxygen. Then monomer was added, and the total mixture was thermostated at 58°C. The initiator was added, dissolved in 10 ml distilled water. The reaction mixture was continuously pumped through the external cell (DMA 401 W) of an Anton Paar Densitometer (DMA 55) by means of a peristaltic pump (flow: ca. 45 ml/min, internal diameter of the butyl rubber tubes 2 mm). Just before entering the densitometer the mixture passed through a heat exchanger inside the cell, thermostated at exactly the same temperature as the reaction vessel, to compensate for any possible heat losses during transport. The temperature during polymerization did not vary more than 0,05°C.

The reaction vessel was kept under a slight excess pressure of nitrogen ($\pm 0,2$ bar) which enabled us to take samples during polymerization. The samples were collected in a flask containing a known amount of hydroquinone to immediately stop the reaction, and their dry solids content was determined. Both methods described (dry solids content of the mixture and its density) were used to calculate conversion-time curves.

RESULTS AND DISCUSSION

Modification of TiO_2 with titanates

The TiO_2 used consists of pure crystalline rutile particles with a z-average diameter of 260 nm, a specific surface area of 7,7 m^2/g and a total pore volume of 0,58 cm^3/g . According to ESCA^{a)} the particle surface consists of pure TiO_2 . It is modified with titanates according to Figure 1. The chemical structure and stability of these titanates were studied before (Refs. 1-2).

^{a)} ESCA = Electron Spectroscopy for Chemical Analysis

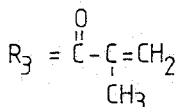
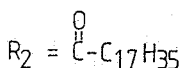
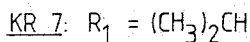
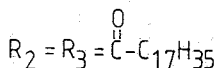
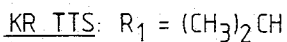


Figure 1. Modification of TiO_2 surface with titanates.

KRTTS contains two long hydrophobic chains that form a hydrophobic mantle round the particle, thus repelling water from the hydrolysable moieties near the particle surface when the TiO_2 is dispersed in water. KR7 only contains one hydrophobic group and therefore is less effective in protecting itself against hydrolysis. By using a mixture of both titanates it is possible to protect the methacrylic acid ester of KR7 at the particle surface against hydrolysis. Best results were obtained by first modifying the TiO_2 with a small amount of KR7, and afterwards with a complementary amount of KRTTS, the total weight percentage of titanate applied being 1%. In this paper we describe polymerizations of MMA^{a)} at the surface of these modified TiO_2 particles. In the case of KRTTS a physical bond between inorganic particle and polymer can be formed. In the case of KR7 the methacrylic acid ester can be considered as a comonomer for polymerization, and thus also a chemical bond between polymer and TiO_2 can be obtained. This can result in a higher polymer content of the

a) methyl methacrylate

inorganic particles: in the case of TiO_2 modified with 0,50 wt% KR7 and 0,5 wt% KRTTS 8,3 wt%, and in the case of TiO_2 modified with 0,80 wt% KR7 and 0,20 wt% KRTTS, 10,5 wt% was found (weight ratio TiO_2 : MMA = 1:3).

On-line conversion measurements

Oscillator based densitometers have been used before for monitoring emulsion polymerizations (Refs. 3-5). Normally it is assumed that the specific volumes of the reaction components are additive and that by mixing no changes in volume occur. Under these assumptions a linear relationship between the specific volume of the reaction mixture and monomer conversion should exist. We studied this relationship for our polymerization systems, in which the differences between the densities of the various components are extremely large (density of TiO_2 is $4,2 \text{ g/cm}^3$, density of MMA = $0,944 \text{ g/cm}^3$). In Figure 2 the specific volume of the total mixture is shown as a function of monomer conversion under various circumstances. The conversion was calculated from the dry solids content of samples taken during polymerization. The polymerizations carried out in this experiment are specified in Table 1.

Table 1. Polymerizations used to study the specific volume of the reaction mixture as a function of conversion under various conditions.

Reaction	Weight ratio KRTTS:KR7	[SDS] (g/l)	[ACPA] (mmol/l)	[MMA] (mol/l)	Stirring Rate rpm
1	1:1	3,0	2,80	0,91	200
2	1:4	3,0	2,70	0,90	200
3	1:1	2,7	2,46	0,90	250
4	1:1	2,4	2,78	0,90	250
5	1:1	2,0	2,76	0,90	250

The TiO_2 content of the mixtures described in this paper was 30,0 g/l.

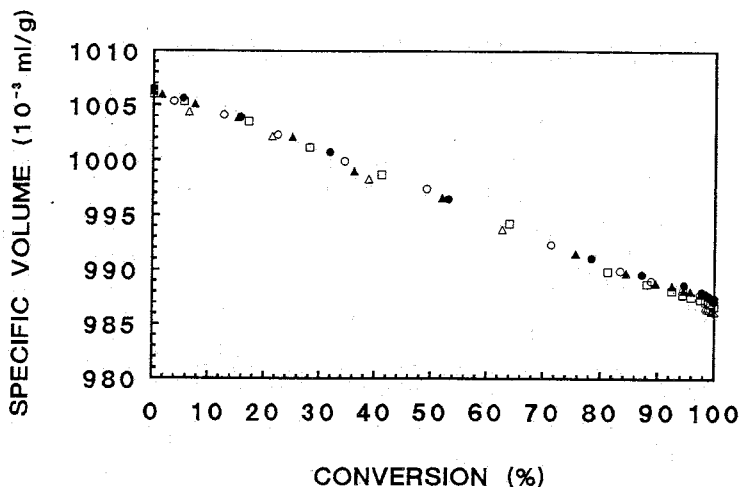


Figure 2. Specific volume of the emulsion as a function of monomer conversion.

● Reaction 1, ▲ Reaction 2, ○ Reaction 3, □ Reaction 4, ▲ Reaction 5.

According to Figure 2 there is a linear relationship between specific volume and conversion in all these systems, independent of reaction conditions like surfactant- or initiator concentration, modification of TiO_2 with different titanates, and stirring speed. Only at very high conversions a small deviation from linearity can be observed, probably caused by volume contraction if monomer is only present in swollen particles (in this stage of the polymerization all monomer droplets will have disappeared). From these experiments it can be concluded that even in this heterogeneous system monomer conversion can be calculated according to the equation derived by F.J. Schork and W.H. Ray (Ref. 4).

$$\chi = \frac{(1/\rho_e^\circ - 1/\rho_e)}{(1/\rho_e^\circ - 1/\rho_e')} \quad (1)$$

where χ is the conversion, ρ_e the density of the reaction mixture and ρ_e° and ρ_e' are the densities at 0 and 100% conversion, respectively.

"Emulsion Polymerizations" of MMA in the presence of modified TiO_2

When hydrophobic TiO_2 particles are dispersed in an aqueous solution of, for instance, SDS, part of the surfactant molecules is adsorbed at the particle surface (Ref. 2). Thus a micelle-like structure with an inorganic particle in the core is formed, in which monomer can be adsorbed. During polymerization the inorganic particle will be encapsulated by a polymer layer. The polymer can be physically bound to the particle and the titanates, but by using a titanate containing a copolymerizable group (like KR7) also a chemical bond between polymer and TiO_2 can be obtained. At a surfactant concentration above cmc^a also "free" micelles, that do not contain an inorganic core, are present, in which polymerization can occur simultaneously. Both polymerizations are competitive as they both need monomer and also surfactant for stabilization. Probably surfactant concentration will play a very important role in the reaction mechanism and kinetics, as was already described for polymerizations on TiO_2 particles modified with KR7TS (Refs. 1-2). Growing particles, consisting of pure polymer and adsorbed monomer, are easily penetrated by monomers, oligomers and radicals, so when a second radical enters the particle immediate termination with the first radical will occur. Therefore, neglecting any possible desorption phenomena, the average number of radicals in such particles (\bar{n}) is $\frac{1}{2}$ ("zero-one system"). In the case of encapsulated TiO_2 particles the inorganic core cannot be penetrated by radicals, so probably these particles can contain more than one radical at the same time ($\bar{n} > 1$). The average life time of radicals at the inorganic surface will be longer than the average life time of radicals in normal polymer particles. Using equation (1) conversion-time curves were calculated from density data obtained for polymerizations at different stirring speeds. As shown in Figure 3 there is an extremely good agreement between the results obtained by this method and the conversion calculated from the dry solids content of the reaction mixture. As expected from Figure 2 only at very high conversions a slight deviation is observed.

a) the critical micelle concentration

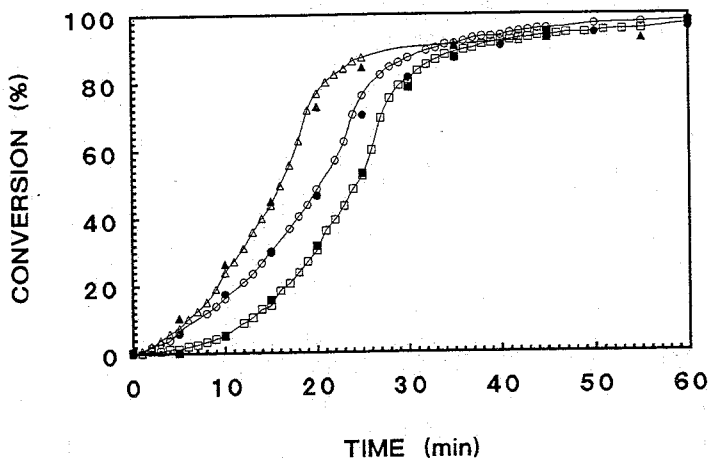


Figure 3. Effect of stirring rate on polymerization kinetics. (MMA concentration = 0,90 mol/l; ACPA conc. = 3,0 mmol/l; SDS conc. = 3,0 g/l; TiO_2 modified with 0,5 wt% KR7 and 0,50 wt% KRITS). Black symbols: according to the dry solids content of the mixture. Open symbols: according to the density of the mixture. □ 200 rpm, ○ 250 rpm, △ 400 rpm.

From Figure 3 it also can be concluded that an increase in stirring rate results in an increase in polymerization rate. In emulsion polymerizations often the opposite effect is observed (Refs. 6-7), but if polymerization can only take place in a small layer at the particle surface (because, like in the case of vinylidene chloride (Ref. 7), the polymer cannot be swollen by its monomer) the same effect is found. This behaviour can be explained by a better dispersion of the TiO_2 particles at a higher stirring rate. Because of this effect a large particle surface is available for polymerization and more radicals will be captured by the TiO_2 particles. Since at their surface termination by other radicals is less probable, the total number of radicals in the system increases, resulting in a higher polymerization rate.

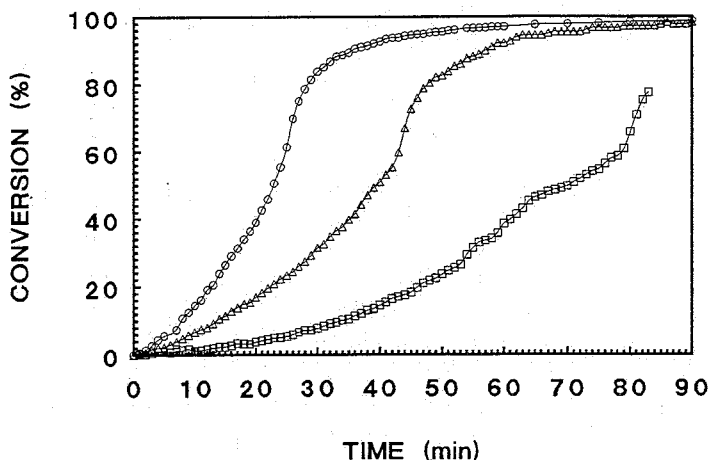


Figure 4. Effect of initiator concentration on polymerization kinetics. (MMA concentration = 0,90 mol/l; SDS conc. = 2,4 g/l; Stirring rate 250 rpm; TiO_2 modified with 0,50 wt% KR7 and 0,50 wt% KRITS).
 □ ACPA conc. = 2,15 mmol/l, Δ 2,46 mmol/l, \circ 2,78 mmol/l.

The initiator concentration appears to have a very large influence on polymerization kinetics as shown in Figure 4. In this case at about 45% conversion a temporary decrease in reaction rate can be observed, followed by a sharp increase. Especially at low initiator concentrations this effect is very clear. In order to avoid the formation of pure polymer particles the surfactant concentration was kept slightly above cmc in this system. Probably during the first part of the polymerization two competitive polymerizations take place: one in free micelles and one at the surface of the modified TiO_2 particles. As all these growing particles need surfactant for stabilization after a while a deficiency of surfactant will arise, resulting in agglomeration of the encapsulated TiO_2 particles. Since they contain a relatively large part of the radicals present in the system, polymerization rate will decrease as these radicals get trapped inside the agglomerates. New radicals are being generated in the water phase and they will cause an increase in

polymerization rate after some minutes. Now polymerization will continue mainly in free polymer particles, formed during the first part of the reaction, and in new particles, formed after the release of surfactant molecules when agglomeration occurs. At a low initiator concentration this effect is more important as the TiO_2 particles contain a relatively larger part of the radicals present in the system (less free polymer particles are formed). If we assume that during the first part of the polymerization reaction mainly takes place at the TiO_2 surface, these experiments can be compared with a seeded emulsion polymerization. However, until 20% conversion polymerization rate is proportional to the 5th power of the initiator concentration, and between 30 and 40% conversion to the 3rd power. In comparison with a normal emulsion polymerization this is extremely high. The assumption of a "seeded polymerization" is not really justified as the TiO_2 particles can only adsorb a very small amount of monomer in a thin layer at the particle surface, and, according to transmission electron microscopy, during this period also particles will be formed by "normal" emulsion polymerization. Because, according to Dark Field Microscopy, also during this period some agglomeration of (encapsulated) particles occurs, the contribution of the normal emulsion polymerization to the polymerization rate will become more important, resulting in the decrease in initiator concentration dependence as observed. After the temporary slowdown the initiator concentration shows only a very small influence on polymerization rate, as expected for an emulsion polymerization. The sharp increase in rate may be explained by the "gel" effect (Ref. 8) or by a net increase of the number of particles.

From the above it can be expected that the surfactant concentration plays a very important role in the kinetical behaviour of these polymerizations. As shown in Figure 3, at surfactant concentrations far above cmc, no special effects are observed. However, a decrease in surfactant concentration appears to influence kinetics during the first part of the polymerization, and, at about the critical micelle concentration (2,0 g SDS/l in this system) also a temporary decrease in polymerization rate at 36% conversion is observed (Figure 5). Similar kinetics have also been observed for polymerizations at the surface of hydrophobic TiO_2 , determined by means of gas chromatography. Also in this case agglomeration of the encapsulated particles may account for the

effect. At high surfactant concentrations the temporary slowdown is not observed, partly because of a better stabilization of the inorganic particles, and partly because the contribution of the normal emulsion polymerization to the conversion-time curves becomes more important, as the number of free micelles increases. In the second part of the polymerization, when reaction mainly takes place in polymer particles, only a small influence of surfactant concentration on polymerization rate can be observed.

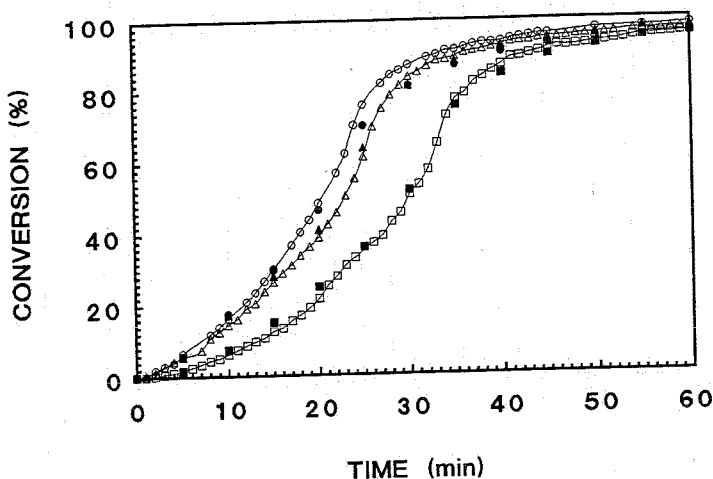


Figure 5. Effect of surfactant concentration on polymerization kinetics. (MMA concentration = 0,90 mol/l; ACPA conc. = 2,8 mmol/l; Stirring rate 250 rpm; TiO_2 modified with 0,50 wt% KR7 and 0,50 wt% KR7S).
 Black symbols: according to the dry solids content of the mixture. White symbols: according to the density of the mixture.
 □ SDS conc. = 2,0 g/l, Δ 2,4 g/l, \circ 3,0 g/l.

In order to prevent agglomeration of the encapsulated TiO_2 particles, without favouring polymerization in free micelles by, for example, adding extra surfactant, the monomer concentration was decreased from 0,90 to 0,30 mol/l. Because of the absence of "large" agglomerates both the polymerization at the TiO_2 surface and the polymerization in free micelles took place during the entire course of the polymerization, and no temporary decrease in reaction rate could be observed (Figure 6).

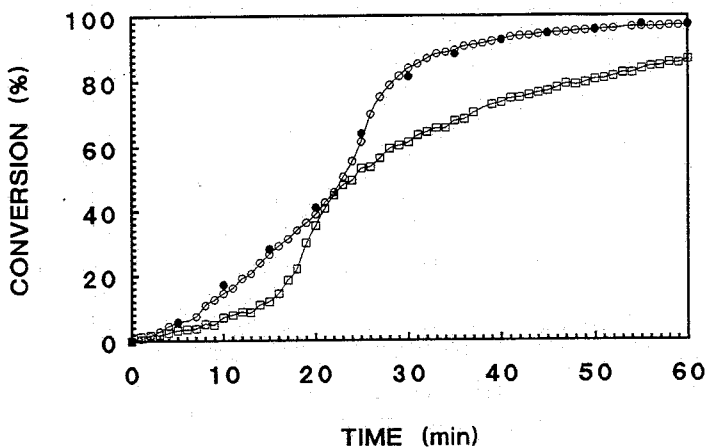


Figure 6. Effect of monomer concentration on polymerization kinetics. (ACPA conc. = 2,8 mmol/l; SDS conc. = 2,4 g/l; Stirring rate = 250 rpm).

Black symbols: according to the dry solids content of the mixture. White symbols: according to the density of the mixture.
 □ MMA conc. = 0,30 mol/l (TiO_2 modified with 0,66 wt% KR7 and 0,34 wt% KRITS).
 ○ MMA conc. = 0,90 mol/l (TiO_2 modified with 0,50 wt% KR7 and 0,50 wt% KRITS).

The final decrease in reaction rate, for most polymerizations at about 80% conversion, was now observed already at 40% conversion. This can be expected, because at this conversion all monomer droplets will have disappeared, as the water solubility of MMA is about 0,15 mol/l. Because less agglomeration occurred, the TiO_2 particles were better encapsulated by polymer and a larger percentage of the polymer was formed at the particle surface (4,3% instead of 2,7% when the weight ratio TiO_2 : MMA is lowered from 1:3 to 1:1 for TiO_2 modified with equal amounts of KR7 and KRITS).

CONCLUSIONS

Polymerizations can be carried out in aqueous dispersions of modified, hydrophobic, submicron inorganic particles (like TiO_2 pigments), stabilized with, for instance, sodium dodecylsulfate. Polymerization can take place at the particle surface, resulting in a particle with an inorganic core and a polymer shell. By using a copolymerizable titanate coupling agent at the TiO_2 surface a chemical bond between particle and polymer can be established. The dispersions show very good stability and, as a result of this, polymerizations can be monitored on-line using a densitometer. There is a linear relationship between the specific volume of the emulsion and the monomer conversion (independent of reaction conditions), and therefore conversion can easily be calculated from density data. Conversion-time curves obtained in this way showed a remarkably good resemblance with those obtained by conventional methods (like the determination of the dry solids content of the mixture). This method enabled us to study the kinetic behaviour of our polymerizations very accurately, and on-line. The polymerizations show very interesting kinetics, highly influenced by variation of initiator or surfactant concentration. Depending on reaction conditions two competitive polymerizations can take place: one at the particle surface and one in free micelles. Both polymerization phenomena are strongly interrelated, in which agglomeration plays a very important role. This agglomeration can be prevented by using low monomer concentrations, resulting in a stable product and a better encapsulation of the TiO_2 particles.

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