

# Formation of grains in a suspension of poly(vinyl chloride)

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A new theory on the formation of poly(vinyl chloride) (PVC) grains in suspension polymerization has been proposed. On agitation, liquid vinyl chloride disperses into water as tiny droplets with diameter of  $\sim 0.7 \mu\text{m}$  where polymerization occurs. These droplets aggregate into PVC grains with diameter of  $\sim 130 \mu\text{m}$  when the rate of conversion reaches  $\sim 25\%$ . This theory is fully verified by a large number of experiments and references.

(Keywords: poly(vinyl chloride); vinyl chloride; morphology)

## INTRODUCTION

The overall structure of the grains of poly(vinyl chloride) (PVC) resin from suspension polymerization is that they have an average diameter of about  $130 \mu\text{m}$  and are composed of primary particles (diameter  $\sim 0.7 \mu\text{m}$ ). The latter consist of domains with diameter of  $\sim 0.015 \mu\text{m}$ . Figure 1 shows a model of such a structure.

There have been differing views about how they are formed. It has been generally considered that all monomers including vinyl chloride (VC), follow the same mechanism of grain formation in suspension polymerization. This mechanism assumes that, on agitation, liquid VC disperses into water as droplets (diameter  $\sim 130 \mu\text{m}$ ) where polymerization occurs. In the droplets PVC macromolecules first precipitate from the monomer due to the insolubility of PVC molecules in VC; they then aggregate into domains, which further agglomerate into primary particles. Finally it is these VC droplets that evolve into the PVC grains (diameter  $\sim 130 \mu\text{m}$ ) when polymerization is complete<sup>1-3</sup>. This mechanism, called the classical theory, is shown in Figure 2.

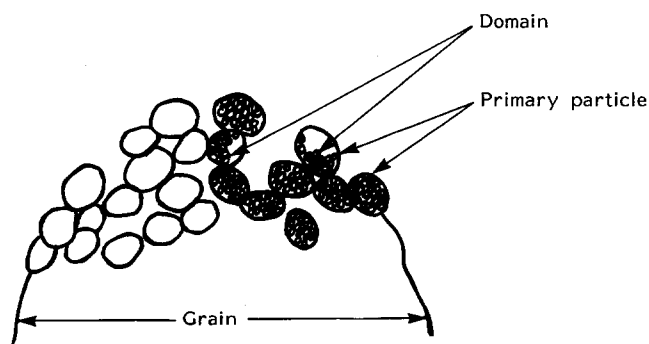


Figure 1 Model of suspension poly(vinyl chloride) (S-PVC) grain structure

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We have disproved this classical theory on the basis of a large number of experiments, and also by reference to data in the literature, and have proposed a new theory<sup>4,5</sup>. According to this new theory, the liquid VC disperses into water as droplets of  $\sim 0.7 \mu\text{m}$  (instead of  $130 \mu\text{m}$ ) where polymerization occurs. These VC droplets aggregate to grains (diameter  $\sim 130 \mu\text{m}$ ) at a conversion of  $\sim 25\%$ . Figure 3 shows the process of grain formation according to the new theory. The mechanism of the formation of the domains in primary particles is that the PVC macromolecules precipitate from VC solution because they cannot dissolve in VC, and then aggregate to form the domains.

## EXPERIMENTAL PROCEDURE

First, 6.5 kg of water, 5.4 g of dicyclohexyl peroxydicarbonate (DCPD), 4.0 g dispersant (respectively methyl cellulose (MC), hydroxyethyl cellulose (HEC), poly(vinyl alcohol) (PVA) or gelatin) and 4.0 kg VC are poured in sequence into a 16 litre stainless-steel vessel. Then the agitator is started at 300 rev/min, and the temperature of the mixture raised. The temperature, pressure and total time of polymerization are  $50^\circ\text{C}$ ,  $7.2 \text{ kg cm}^{-2}$  and 6 h respectively. The mixture is taken out of the vessel when

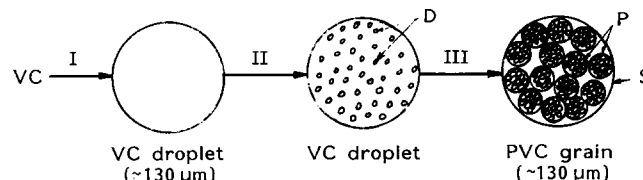
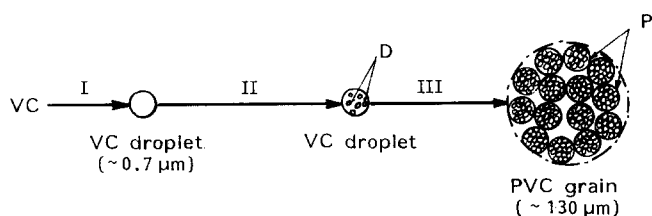


Figure 2 Schematic representation of the classical theory. (I) Agitate. (II) Polymerize and PVC macromolecules precipitate and aggregate. (III) PVC domains aggregate to PVC primary particles, polymerization completes. D = domains; P = PVC primary particles; S = skin of grain

**Table 1** Results of PVC grains in suspension using an optical microscope (at magnification  $\times 450$ )

Name and amount of dispersant (based on VC)	Diameter of grains ( $\mu\text{m}$ )			
	$\geq 250$	149–250	88–149	74–88
Gelatin, 0.1%	Skin	Skin	Skin	Appears to be skin-free
Poly(vinyl alcohol), 0.1%	Appears to be skin-free	Skin-free	Skin-free	Skin-free
Hydroxyethyl cellulose, 0.1%	Appears to be skin-free	Appears to be skin-free	Appears to be skin-free	Appears to be skin-free
Methyl cellulose, 0.05% and hydroxyethyl cellulose, 0.05%	Appears to be skin-free	Appears to be skin-free	Appears to be skin-free	Appears to be skin-free
Methyl cellulose, 0.1%	Appears to be skin-free	Skin-free	Skin-free	Skin-free
Methyl cellulose, 0.5%	Skin	Skin	Skin	Skin-free
Methyl cellulose, 1.0%	Skin	Skin	Skin	Skin

**Figure 3** Schematic representation of the new theory. (I) Agitate. (II) Polymerize and PVC macromolecules precipitate and aggregate. (III) VC droplets agglomerate at  $\sim 25\%$  conversion, polymerization completes. D = domains; P = PVC primary particles

the polymerization is complete and the pressure reaches  $5.0 \text{ kg cm}^{-2}$ . The product is separated by centrifuging, and washed and dried. Finally, PVC resin with a viscosity of  $1.90\text{--}2.10 \text{ cP}$  is obtained.

We have examined these PVC resins by optical microscopy and electron microscopy. The results are shown in *Table 1* and *Figure 4*.

## RESULTS AND DISCUSSION

### *A large number of suspension PVC grains are skin-free*

Those grains whose interior microstructure can be seen through the surface are called skin-free grains<sup>4,6,7</sup>, while the others are called skin grains. The observations from optical microscopy are summarized in *Table 1* and the electron micrographs are shown in *Figure 4*.

According to the classical theory, skin should be formed on the surface of the PVC grains because the surface of the VC droplets ( $\sim 130 \mu\text{m}$ ) in contact with the aqueous phase absorb dispersant dissolved in water at the initial stage of polymerization and graft copolymerization of the VC to the dispersant occurs. Hence the classical theory cannot explain the existence of skin-free grains. However, the new theory can. According to the new theory, it is the VC droplets of  $\sim 0.7 \mu\text{m}$  that adsorb the dispersant at the initial stage of polymerization to form the grains. If there remains a large amount of dispersant in the water after forming grains, the dispersant will be continually adsorbed by the PVC grains to form the skin of the grains; and if there is only a little amount of dispersant left in the water, an observable skin cannot be formed on the surface of the grains. Skin-free PVC grains have also been observed by other investigators<sup>1,8</sup>.

### *Influence of rotary speed of agitator on diameter of primary particles*

The phenomenon that the diameter of primary particles decreases with the increase of the rotary speed of the

**Table 2** Relationship between the diameter of the primary particles and the rotary speed of agitation<sup>1</sup>

Speed of agitator (rev/min)	Average diameter of the primary particles ( $\mu\text{m}$ )
100	2.0
150	1.7
200	1.5
250	1.0
330	0.8
400	0.6

agitator has been noted by us<sup>4</sup> as well as by Pan and others<sup>1,9</sup>. The data showing this relationship are shown in *Table 2*.

The classical theory cannot provide a satisfactory explanation of this phenomenon. However, the new theory can. According to this new theory, the basic moving units in this system at the initial stage of polymerization are the VC droplets of  $\sim 0.7 \mu\text{m}$ , which finally evolve into the PVC primary particles of  $\sim 0.7 \mu\text{m}$  when polymerization is complete, so the diameter of the primary particles is certainly influenced by changing the rotary speed of the agitator.

### *Influence of emulsifier on diameter of primary particles*

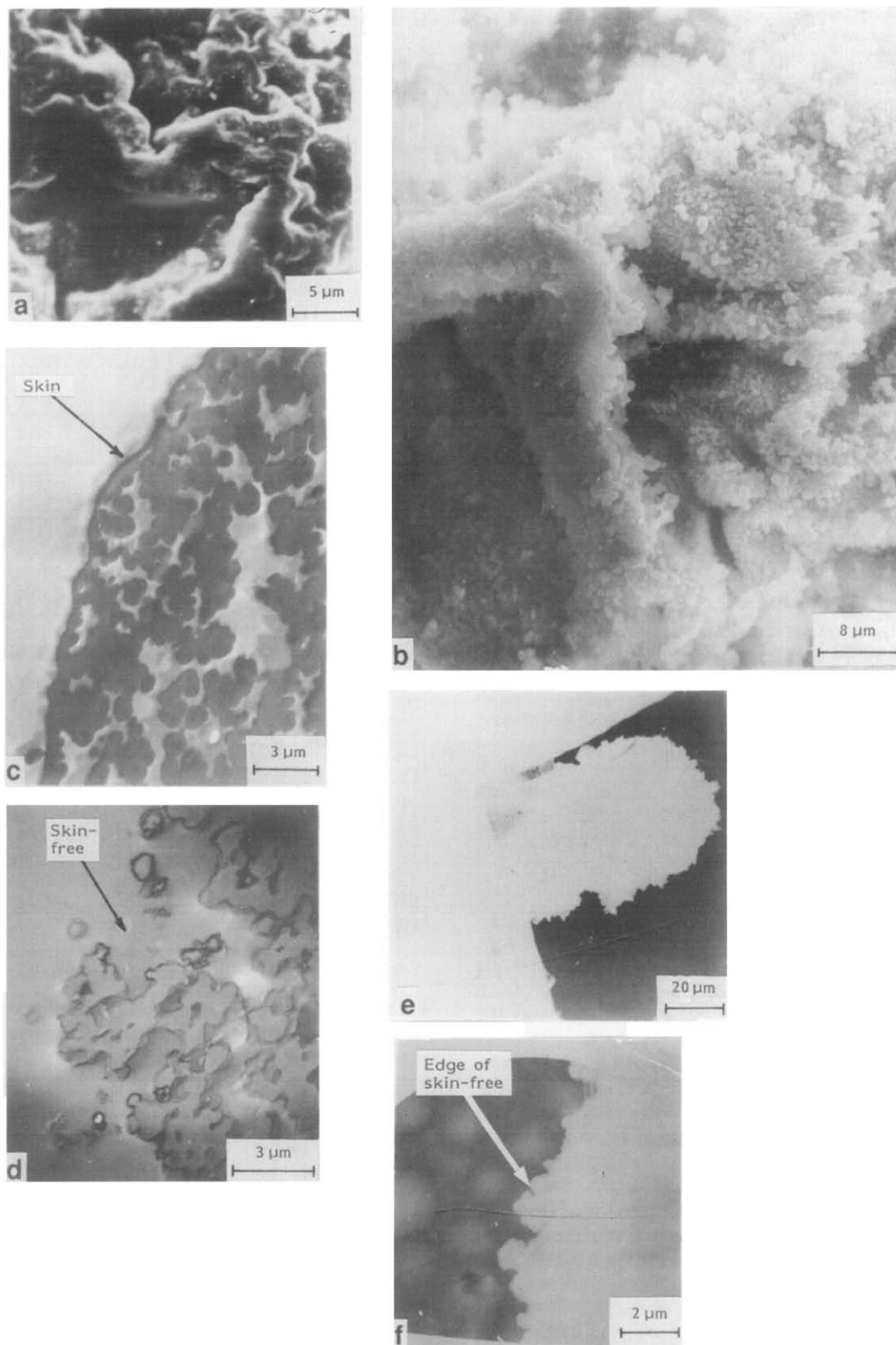
The fact that the presence of the emulsifier can cause a decrease in the diameter of the primary particle has also been noted by us<sup>4</sup> and by others<sup>1,9</sup>.

According to the new theory, the VC droplets of  $\sim 0.7 \mu\text{m}$ , which finally evolve into the  $\sim 0.7 \mu\text{m}$  PVC primary particles, are the basic moving units at the initial stage of polymerization. The addition of the emulsifier causes the decrease of interfacial tension in the system, which makes the diameter of VC droplets decrease, and therefore the diameter of the primary particles decreases. However, according to the classical theory, it can only cause a decrease of the diameter of the grains, for the basic moving units in the whole polymerization process are the  $\sim 130 \mu\text{m}$  VC droplets, which finally evolve into the PVC grains when the polymerization is complete.

### *The primary particles also have skin*

Our group<sup>7</sup> and Krzewki *et al.*<sup>10</sup> have observed that the primary particles also have skin (*Figure 5*).

According to the new theory, the VC droplets of  $\sim 0.7 \mu\text{m}$ , which evolve into the  $\sim 0.7 \mu\text{m}$  PVC primary particles when the polymerization is complete, exist in aqueous phase as basic units before the agglomeration, and the dispersant in water is adsorbed onto the surface of the  $0.7 \mu\text{m}$  droplets to form the skin. However,



**Figure 4** Micrographs of skin and skin-free S-PVC grains. (a) SEM micrograph of the skin grains. (b) SEM micrograph of the skin-free grains. (c) TEM micrograph of the skin grains. (d) STEM micrograph of the skin-free grains. (e) TEM picture of a single skin-free grain. (f) TEM picture showing the discontinuous edge of the skin-free grains

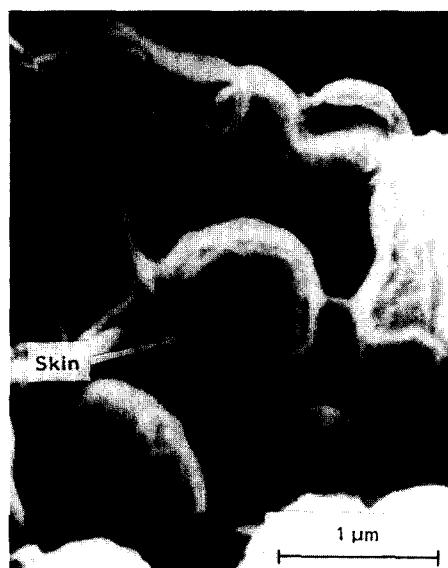


Figure 5 SEM micrograph of the skin primary particles

Table 3 Relationship between specific surface and conversion<sup>11</sup>

Conversion (%)	Specific surface (m <sup>2</sup> g <sup>-1</sup> )
12.5	2.3
12.6	2.1
14.3	2.9
18.5	2.2
20.8	1.5
21.8	2.3
37.7	0.75
54.0	0.70
59.2	0.70
61.5	0.50
63.6	0.30
72.7	0.40
77.6	0.24
83.2	0.28
84.7	0.40
88.5	0.25

according to the classical theory, the primary particles should never have a skin because they do not contact with water at all.

#### Relationship between conversion and specific surface of PVC resin

The relationship between the specific surface and the conversion of the PVC resin has been determined by Ravey *et al.*<sup>11</sup>. The results are shown in Table 3. A sharp change of the specific surface is noticed at a conversion between 21.8% and 37.7%.

This phenomenon can be explained reasonably only by the new theory. Before ~25% conversion (i.e. before the VC droplets agglomerate to grains), the specific surface of the PVC resin is that of the VC droplets of ~0.7 μm. If the VC droplets are taken as solid spherules with diameter of 0.7 μm, the calculated result for the specific surface is 6.1 m<sup>2</sup> g<sup>-1</sup>. The practical values shown in Table 3 are lower than the calculated values because the VC droplets partially coalesce. But after agglomeration, the specific surface of the PVC resin should be that of the grains. If the grains are considered as solid spherules with diameter of 130 μm, the calculated result of the specific surface is 0.033 m<sup>2</sup> g<sup>-1</sup>. But actually the PVC grains,

especially the skin-free grains, are not all solid spherules (see Figure 4); they are porous grains, so the measured value in Table 3 is higher than the calculated value.

#### Relationship between concentration of dispersant and conversion

A sudden change has been found on the curve of concentration of dispersant agent vs. conversion of polymerization within the range 15–30% conversion by Cheng<sup>12</sup> (see Figure 6). Before 15–30% conversion, the concentration of hydroxypropylmethyl cellulose (HPMC) in the polymerization aqueous phase decreases dramatically with the increase of conversion; after 15–30% conversion, it decreases gently. A similar characteristic of PVA has been found by Xu *et al.*<sup>13</sup>.

According to the new theory, this phenomenon is related to the agglomeration of VC droplets at ~25% conversion. Before agglomeration, it is the VC droplets with large specific surface (1.5–2.9 m<sup>2</sup> g<sup>-1</sup>) that adsorb the dispersant dissolved in water, so the concentration drops rapidly. However, after agglomeration, it is the grains with small specific surface (0.25–0.75 m<sup>2</sup> g<sup>-1</sup>) that adsorb the dispersant in water, so the concentration decreases gently (see Table 3). The classical theory cannot be applied to explain the phenomenon.

#### Relationship between interfacial tension and polymerization time

There is a sudden change on the curve of interfacial tension vs. polymerization time when time is in the range of 1.5–2.0 h (Figure 7). We suggest that ~25% conversion is reached when the polymerization proceeds for 1.5–2.0 h, and agglomeration of VC droplets occurs at this moment. It is well known that the interfacial tension increases as the result of the decreased concentration of dispersant in water. It is due to the fact that the concentration of the dispersant in water changes suddenly at ~25% conversion (Figure 6), so a sharp change of the interfacial tension in the system appears in the time range of 1.5–2.0 h.

The classical theory cannot explain this sharp change.

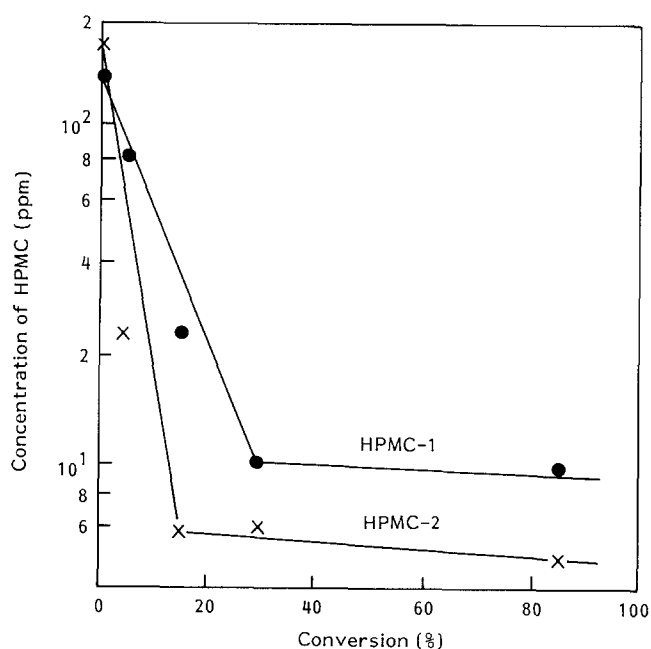


Figure 6 Concentration of HPMC vs. conversion of polymerization

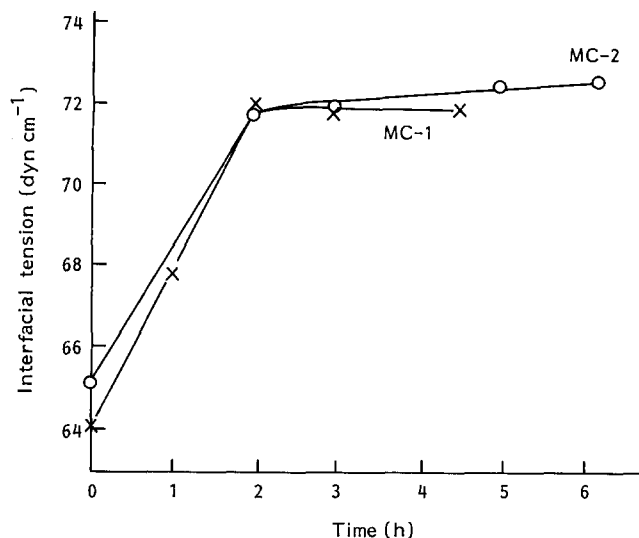


Figure 7 Interfacial tension vs. polymerization time (methyl cellulose (MC) is the dispersant)

Table 4 The influence of agitation on the properties of PVC resin

Sample no.	1	2	3	4	5	6
Stopping time of agitation (h)	0	0.5	1.0	2.0	3.0	4.0
Conversion when restarting agitator (%)		9.3	15.4	26.8	39.5	61.1
Amount deposited on the wall of vessel (part)	8.3	8.0	7.2	0.2	1.0	56.8
Gelatination (fish eye) (piece)	83	76	102	52	69	202
Uniformity of grain size (%)						
60 mesh	10.0	10.0	10.0	99.9	100.0	74.5
100 mesh	88.3	91.0	86.5	93.5	90.0	63.0
200 mesh	47.0	50.5	41.8	39.9	45.3	55.5

#### Influence of 'on' and 'off' of the agitator on properties of PVC resin

The following experimental result is reported in a patent<sup>14</sup>. First, 700 parts of water, 300 parts of vinyl chloride (VC), 0.9 parts of methyl cellulose (MC) and 1.5 parts of lauroyl peroxide are mixed in a stainless-steel polymerization vessel (2 litres). The mixture is pre-agitated for 30 min at a speed of 200 rev/min. When the temperature reaches 56°C, polymerization starts. After an hour, the stirring is stopped for a period of time, and then restarted until polymerization is complete. It is observed that the properties of the resin vary with different periods of stopping time before restarting agitation. All results are shown in Table 4.

It can be seen in Table 4 that if the stirring is restarted at 26.8% conversion, the amount deposited is small and the gelatination (fish eye) of resin is at its minimum; if the stirring is restarted at 15.4% or 39.5% conversion, its amount deposited and the gelatination (fish eye) increases. Obviously, this is related to the agglomeration of VC droplets occurring at ~25% conversion.

According to the new theory, if the agitator is restarted at 26.8% conversion, the agglomeration of the VC droplets occurs in the absence of the disturbance of agitation. The PVC grains have uniform size and

porosity, so there are less fish eyes; and the grains cannot coalesce because the agitator is restarted just after agglomeration. Moreover, without agitation, the VC droplets are more likely to agglomerate to grains than to deposit towards the surface of the vessel. So the amount deposited is the least. But if the agitator is restarted at  $\geq 39.5\%$  conversion, the PVC grains formed by the primary particles will coalesce into bigger grains or blocks easily and deposit on the surface of the vessel easily, because there is no agitation. If the agitator is restarted at  $\leq 15.4\%$  conversion, or the agitator does not stop, the agglomeration of the VC droplets will be disturbed by agitating. The properties of PVC will thus get worse, and the amount deposited will increase (see Table 4).

#### Relationship between polymerization time and coalescence

We have found that if the amount of dispersant agent used in the system is much smaller and the polymerization period is long, the polymer coalesces; coalescence does not appear if the period is short.

According to the new theory, the time needed to reach ~25% conversion is short if the polymerization period is short. Therefore, the amount of dispersant adsorbed by the VC droplets is small, and the amount left in the aqueous phase is large. The large amount of dispersant left in water will continuously be adsorbed by the grains to form the skin, which can prevent the grains from aggregating into big blocks. On the other hand, the time needed to reach ~25% conversion is long if the polymerization period is long, so the amount of dispersant adsorbed by the VC droplets is large and the amount left in water is small. The small amount of dispersant left in water will be insufficient to form a strong skin on the grains. The grains therefore coalesce into big blocks easily.

This phenomenon cannot be explained by the classical theory either.

#### A large amount of dispersant agent exists in PVC grains

The presence of a large amount of dispersant in PVC grains is found by Cheng<sup>12,15</sup>. In his opinion, this is caused by the solubility of dispersant in VC. We disagree with this opinion. We suggest that, since the molecule of dispersant consists of hydrophilic and oleophilic groups at the same time, there exists an inexorable thermodynamic tendency at the oil/water interface.

The new theory can give a very satisfactory explanation of this phenomenon. Because the dispersant is adsorbed by the VC droplets, which evolve into the primary particles when the polymerization is complete, so after agglomeration the adsorbed dispersant exists in the grains that are formed by the primary particles. This does not depend at all on whether dispersant can dissolve or not in VC.

#### Comparison of diameter of PVC primary particles in suspension and emulsion polymerization

To compare the data shown in Table 5, we might conclude that the size of initial droplets (i.e. primary particles) in suspension polymerization can be analogous to that in emulsion polymerization.

We have assumed that a polymerization system with a total weight  $G$  is an isolated system of small droplets. In this system, the large amount of surface energy as the

**Table 5** Comparison of the diameter of PVC primary particles in suspension and emulsion polymerization

	Suspension	Emulsion
Medium of dispersant	Water	Water
Stabilizer	Dispersant	Emulsifier
Surface tension of aqueous phase at beginning of polymerization (dyn cm) <sup>-1</sup>	45–60	30–40
Rotary speed of agitator (rev/min)	300	300
Diameter of the primary particles (μm)	0.5–1.5	0.15–0.40

result of agitation remains in balance with the agitation work during the whole process of polymerization. If the rotary speeds of agitator in suspension and emulsion are both 300 rev/min (see Table 5), the agitation work in both systems can be regarded as equal. Hence the surface energies in both systems are also equal. Therefore, the following equation can be proposed:

$$S_e \gamma_e = S_s \gamma_s = W \quad (1)$$

where  $S_e$  is the total surface area of PVC primary particles in emulsion system,  $S_s$  is the total surface area of PVC primary particles in suspension system,  $\gamma_e$  is the surface tension of emulsion,  $\gamma_s$  is the surface tension of suspension and  $W$  is the agitation work.

From the electron micrographs, we have noted that the shape of all PVC primary particles in suspension or in emulsion are basically spherical. If the weight of a system (suspension or emulsion) is  $G$ , then:

$$S = \frac{G}{\frac{1}{6}\pi D^3 \rho} \pi D^2 = \frac{6G}{D\rho} \quad (2)$$

where  $S$  is the total surface area of PVC primary particles in a system,  $\rho$  is the specific gravity of PVC resin and  $D$  is the diameter of PVC primary particles.

From equations (1) and (2), if we take the same weight from the suspension system and emulsion system, the diameters of the PVC primary particles in suspension  $D_s$  can be calculated by:

$$D_s = D_e \gamma_s / \gamma_e \quad (3)$$

where  $D_e$  is the diameter of primary particles in emulsion.

The diameter of PVC primary particles in emulsion  $D_e = 0.15\text{--}0.40 \mu\text{m}$  with average value of  $0.28 \mu\text{m}$  is commonly accepted (Table 5). If  $\gamma_e = 35 \text{ dyn cm}^{-1}$  and  $\gamma_s = 53 \text{ dyn cm}^{-1}$ ,  $D_s = 0.42 \mu\text{m}$  can be obtained from equation (3)<sup>16</sup>.

The calculated value is basically consistent with the experimental result and in contradiction with the classical theory ( $\sim 130 \mu\text{m}$ ).

## CONCLUSION

The new theory can be applied to explain all the experiments of suspension polymerization, whereas the classical theory is often confronted with difficulties.

## ACKNOWLEDGEMENTS

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