

# Particle Features of Poly(vinyl chloride) Resins Prepared by a New Heterogeneous Polymerization Process

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**ABSTRACT:** The heterogeneous polymerization of vinyl chloride monomer (VCM), with *n*-butane as the reaction medium, was used to prepare poly(vinyl chloride) (PVC) resins. The particle features of the resulting resins and the particle formation mechanism of the polymerization process were investigated. The PVC resins prepared by the new polymerization process had a volume-average particle size comparable to that of suspension PVC resins and a lower number-average particle size. From scanning electron micrographs, it could be seen that the new PVC resins had a regular particle shape and a smooth surface with no obvious skin. They also had a high porosity. The new PVC resins were composed of individual and loosely aggregated primary particles. The diameter of the primary particles in the top layer of the grains was smaller than that of the primary

particles in the center part of the grains. On the basis of the particle features of these PVC resins, a particle formation mechanism for the new polymerization process was proposed. PVC chains precipitate from a VCM/*n*-butane mixed medium to form primary aggregates at a very low conversion, and the primary aggregates of the PVC chains aggregate to form primary particles, which further aggregate to form grains. The primary particles and grains grow by the capture of newly formed PVC chains and their primary aggregates and by polymerization occurring inside the aggregates. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 954–958, 2003

**Key words:** heterogeneous polymers; morphology; poly(vinyl chloride) (PVC); particle nucleation

## INTRODUCTION

Approximately 80% of the total demand for poly(vinyl chloride) (PVC) is satisfied by the suspension polymerization process. In this process, vinyl chloride monomer (VCM) is suspended, as liquid droplets, in a continuous water phase by a combination of vigorous agitation and the presence of a suspending agent or agents. Because PVC is effectively insoluble in its own monomer, PVC chains start to precipitate from the monomer phase at a very low conversion (<0.1% conversion), forming a separate phase (polymer-rich) inside the droplets. The precipitating chains aggregate to form microdomains, which are unstable and rapidly aggregate to give domains. The further aggregation or growth of domains results in the formation of primary particles. The primary particles grow with conversion at almost the same rate by the accretion of microdomains or domains onto their surface as they do by polymerization inside the primary particles. As the primary particles increase in size and the volume fraction of the polymer phase increases, aggregation

will involve multiparticle contacts and result in a decrease in the primary particle number and the formation of a continuous network of primary particles throughout the polymer particle/monomer droplet. At the later stage of polymerization (when the monomer phase disappears), further polymerization leads to the fusion of primary particles and the formation of agglomerates.<sup>1–6</sup>

As a direct result of this process and the density difference between PVC and VCM, PVC grains with unique morphology and porosity can be formed. The morphology and porosity of suspension PVC resins depend on many polymerization factors, such as the type and concentration of the suspending agent or agents,<sup>6–11</sup> the agitation,<sup>12–16</sup> the polymerization temperature, and the conversion.<sup>5,17,18</sup> These features influence the content of the residual monomer and the processing properties of PVC resins.<sup>1–3</sup> Requirements for PVC resins have changed very much since the 1970s. This has been brought about by a number of factors, one of the most important being the toxicity of VCM, which has led to a reduction in the unreacted monomer. Several technological improvements have been advanced to meet this requirement, such as using composite suspending agents and adding oil-soluble surfactants to the VCM suspension process to produce higher porosity resins from which it is easier to strip

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TABLE I  
Recipes and Conditions for VCM Heterogeneous Polymerizations

Run	Initial weight (g)				Protective colloid	Polymerization time (min)	Conversion (%)
	VCM	Water	<i>n</i> -Butane	Initiator			
S1	172.0	360.0	—	0.25	0.36	485	81.7
H1	152.0	—	162.5	1.50	0.60	360	61.8
H2	175.0	—	122.5	2.00	0.60	360	76.5
H3	159.0	—	123.5	2.50	0.60	300	73.6
H4	185.0	—	135.5	3.00	0.60	120	41.6
H5	183.5	—	133.4	3.00	0.60	240	69.2
H6	180.0	—	133.5	3.00	0.60	360	81.7

unreacted VCM.<sup>1,3,19–22</sup> Other ways should be developed to meet this requirement.

A new VCM heterogeneous polymerization process, with *n*-butane as a reaction medium, was developed to prepare porous PVC resins with excellent monomer removal and processing properties. The equilibrium behavior of VCM/*n*-butane and the kinetic features of the new VCM polymerization process were reported in a previous article.<sup>23</sup> The aim of this study was to investigate the particle features of PVC resins and the particle formation mechanism of the new VCM polymerization process.

## EXPERIMENTAL

VCM and *n*-butane were supplied by EVC, Ltd. (Runcorn, UK), and Linde Gas, Ltd. (Stoke-on-Trent, UK), respectively. Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, used as an initiator, was supplied by Akzo Nobel Co. (Gillingham, UK) under the trade name Perkadox 16S (95% purity). Sorbitan monosterate (Span 60) and poly(vinyl alcohol) (PVA; trade name Alcotex72.5), used as protective colloids, were supplied by Sigma Chemical Co. (Gillingham, UK) and Harlow Chemical Co., Ltd. (Harlow, UK), respectively.

VCM polymerizations were carried out in a 1.0-L jacketed glass autoclave (Buchi AG from Ken Kimble Co., Seven Oaks, UK) fit with four equally spaced baffles about 7 mm wide and an agitator consisting of a six-flat-blade turbine. For VCM polymerizations with *n*-butane as the reaction medium, the initiator and Span 60 surfactant were added to the reactor before it was closed. The reactor was checked for leaks, and nitrogen and oxygen in the reactor were removed through the addition and venting of *n*-butane several times. After the reactor was charged with *n*-butane and VCM, the mixture was agitated for about 20 min at room temperature to dissolve the initiator and surfactant; then, it was heated up to the polymerization temperature. The timing of the polymerization was started when the temperature achieved the required value (45°C). The polymerization temperature was then well controlled. At the end

of the polymerization, the reactor was cooled quickly with cold water (<10 min for cooling to room temperature). The unreacted VCM and *n*-butane were vented at room temperature initially, and then the reactor was heated up to about 60°C to remove VCM and *n*-butane more completely. The dried PVC resin was obtained and weighed. The final conversion was calculated from the weights of the resulting resin and the charged VCM. The VCM suspension polymerization was performed in the usual way, and PVA was used as a suspending agent. The recipes and conditions of the VCM polymerizations are shown in Table I (S1 presents a suspension polymerization with PVA as the protective colloid, and H1–H6 present the new heterogeneous polymerizations).

## Characterization of the PVC resin

The particle size of the PVC samples was measured with a Coulter laser size analyzer (Luton, UK).

The porosity of the PVC resins was characterized by the cold plasticizer absorption (CPA). A weighed amount of a PVC resin was placed in a sand-core tube and was allowed to absorb dioctyl phthalate (DOP) plasticizer at room temperature (20 ± 2°C) for 30 min. The unabsorbed DOP was removed by centrifugal separation (at 3000 rpm for 60 min).

PVC grains were sectioned directly and gold-coated *in vacuo*. The morphology of the PVC grains was observed with a Philips XL30 scanning electron microscope (FEI, Shanghai, China).

## RESULTS AND DISCUSSION

### Particle size and porosity of the PVC resins

The number-average particle size ( $D_n$ ), volume-average particle size ( $D_v$ ), and 50% volume accumulation particle size ( $D_{50}$ ) of the PVC resins obtained from the particle size measurements are shown in Table II.  $D_v$  and  $D_{50}$  of the H series PVC resins are comparable to those of suspension PVC, but  $D_n$  of the H series PVC resins is much smaller than that of suspension PVC.

TABLE II  
 $D_w$ ,  $D_v$ ,  $D_{50}$ , and CPA of the PVC resins

Run	$D_n$ ( $\mu\text{m}$ )	$D_v$ ( $\mu\text{m}$ )	$D_{50}$ ( $\mu\text{m}$ )	CPA (g/100 g of PVC)
S1	9.11	130.6	121.6	32.9
H1	0.938	154.3	155.5	83.4
H2	1.00	207.6	203.5	63.7
H3	0.936	168.3	166.5	68.3
H4	0.918	209.5	190.0	129.4
H5	0.924	212.7	203.1	76.2
H6	1.352	215.8	206.8	67.5

This shows that many small particles exist in PVC resins prepared by the new polymerization process, but their volume or weight fraction is very low. The existence of small particles is related to the particle features of the PVC resins and the mechanism of the new polymerization process, which is discussed later.

CPAs of PVC resins are also given in Table II. Those of the H series PVC resins are greater than that of S1 PVC, even for the H6 PVC resin, which has a conversion similar to that of the S1 PVC. This shows that PVC prepared by the new polymerization process has a higher porosity than that of suspension PVC (the CPA of S1 PVC is higher than that of most commercial suspension PVC resins). By comparing the CPAs of PVCs from H2 and H3, we can see that the PVC resin prepared with a greater *n*-butane/VCM ratio in the recipe has a higher porosity when the conversions are similar. From CPAs of H4, H5, and H6 PVCs, it can be seen that the porosity of a PVC resin decreases with an increase in the conversion when the *n*-butane/VCM ratio is almost constant.

### Particle morphology of the PVC resin

Typical scanning electron microscopy (SEM) micrographs for the whole grain and for the top layer of a sectioned PVC grain prepared by the new polymerization process (H6) are shown in Figures 1 and 2. An SEM

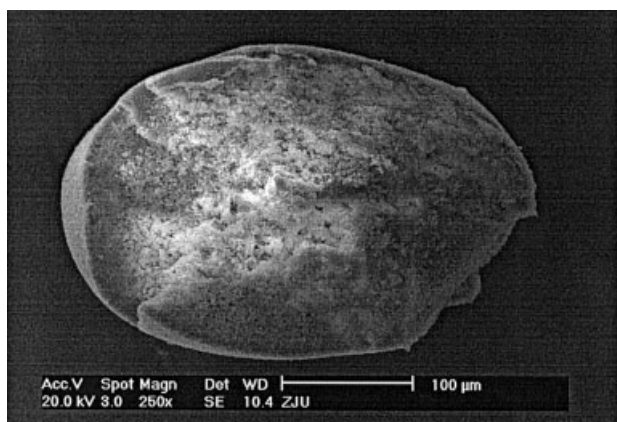


Figure 1 SEM micrograph of the entire section of an H6 PVC grain.

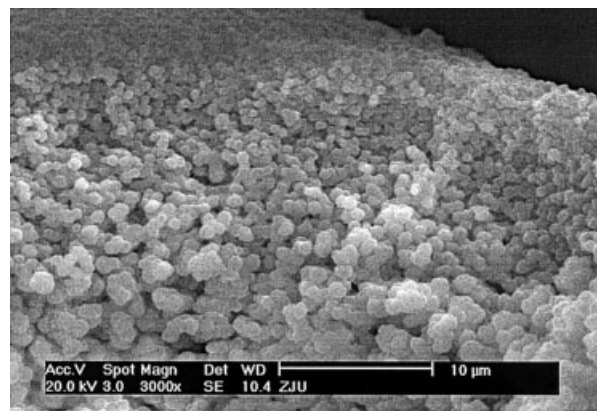


Figure 2 SEM micrograph of the top-layer section of an H5 PVC grain.

micrograph of a suspension PVC (S1) grain is shown in Figure 3. By comparing Figures 1, 2, and 3, we can see that the morphology of the PVC grains prepared by the new polymerization process is quite different from that of suspension PVC. First, the particle shape of the PVC resin prepared by the new polymerization process is more regular than that of suspension PVC, and the surface is smooth. Second, the PVC resin prepared by the new polymerization process does not have a continuous and dense skin surrounding the grain, whereas the suspension PVC grain is surrounded by a skin or pericellular membrane. Finally, the PVC resin obtained from the new polymerization process is composed of a great number of fine primary particles that are not fused together, whereas the suspension PVC resin is composed of primary particles that are almost completely fused together (agglomerates of primary particles). From Figure 2, it can also be seen that the sizes of the primary particles in the PVC resin prepared by the new polymerization process are not identical. The primary particles in the top layer of the grain are smaller than those in the center of the grain. Therefore, the top layer is denser than the center part of the grains, as shown in Figure 1.

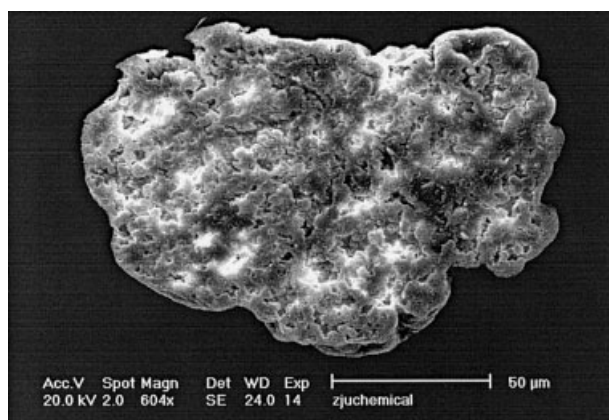
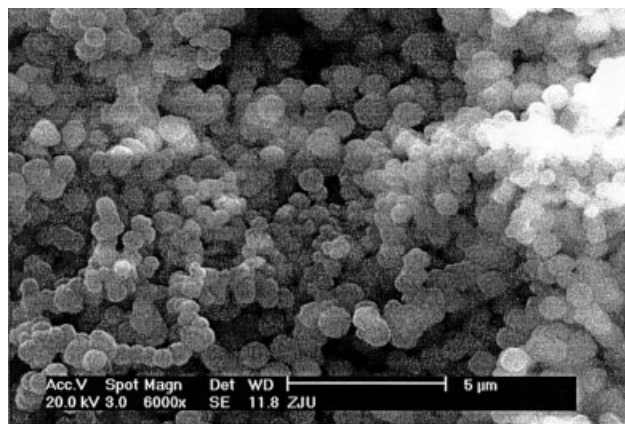
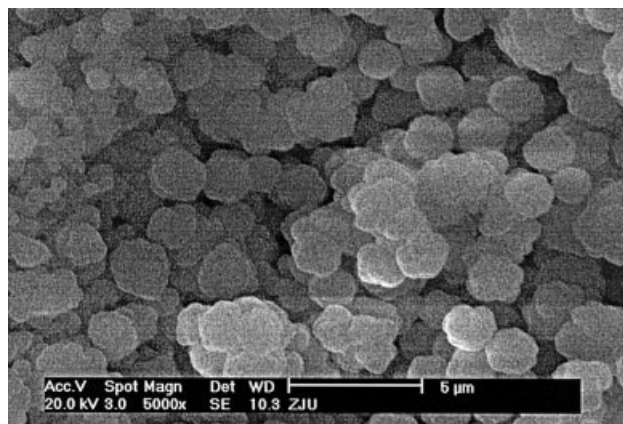


Figure 3 SEM micrograph of the entire section of an S1 PVC grain.



**Figure 4** SEM micrograph of the center part of a sectioned H4 PVC grain.



**Figure 6** SEM micrograph of the center part of a sectioned H6 PVC grain.

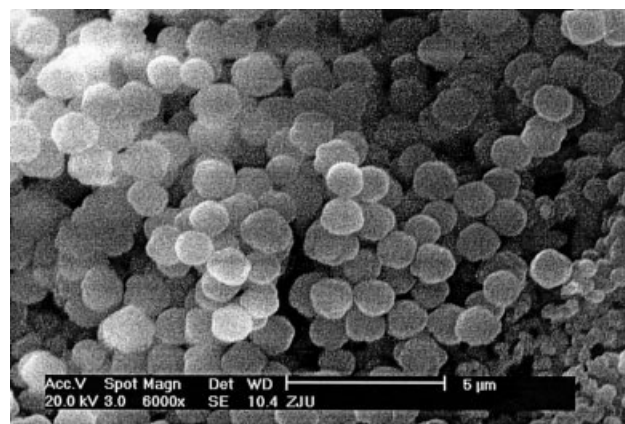
SEM micrographs of the center parts of sectioned H4, H5, H6, and S1 PVC resins with a higher magnification are shown in Figures 4–7. The PVC resins prepared by the new polymerization process are clearly composed of many individual primary particles and some looser aggregates of primary particles, whereas the suspension PVC is mainly composed of fused primary particles. Moreover, the PVC resins prepared by the new polymerization process have a higher porosity than the suspension PVC resin. From micrographs of H4, H5, and H6 PVC resins, we can see that the size of the primary particles and the aggregation degree of the primary particles increase, and the porosity decreases, with an increase in conversion when the *n*-butane/VCM ratio is almost constant.

#### Particle formation mechanism of the new VCM polymerization process

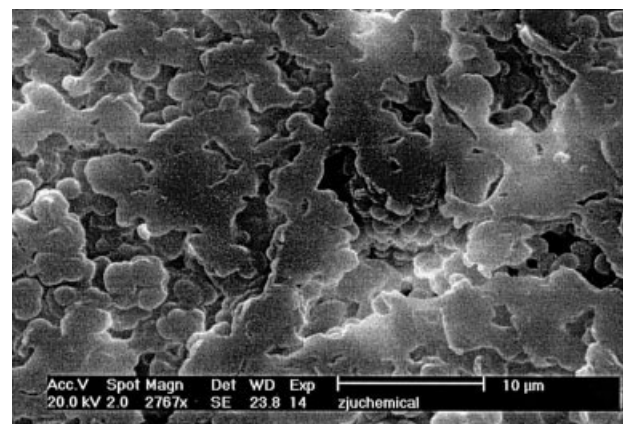
The aforementioned differences in the particle features between the suspension PVC resin and PVC resin prepared by the new polymerization process can be

related to the particle formation mechanisms of the two polymerization processes. The particle formation mechanism of VCM suspension polymerization has been well studied from microscopic and macroscopic viewpoints.<sup>1–5</sup> The irregular shape of suspension PVC grains is caused by the coalescence and shrinkage of polymer-containing VCM droplets during the polymerization process. The presence of a skin is caused by the graft copolymerization of VCM to the suspending agent (PVA in this study), which occurs at the VCM/water interface. The fusion of primary particles can occur because the glass-transition temperature of VCM-swollen PVC is lower than the polymerization temperature.<sup>24</sup>

For VCM polymerization with *n*-butane as the reaction medium, VCM and *n*-butane are miscible over the entire composition range, and the reaction system is homogeneous and transparent initially. As the polymerization is started by the oil-soluble initiator, PVC chains start to precipitate from the VCM/*n*-butane mixture at a very low conversion because the solubility parameter difference between PVC and the VCM/



**Figure 5** SEM micrograph of the center part of a sectioned H5 PVC grain.



**Figure 7** SEM micrograph of the center part of a sectioned S1 PVC grain.

*n*-butane mixture is even greater than that between PVC and VCM [the solubility parameters of *n*-butane, VCM, and PVC are 6.80, 7.80, and 9.7 (cal/mL)<sup>1/2</sup>, respectively].<sup>25</sup> The precipitating PVC chains aggregate to form very small particles (like microdomains, the domains in VCM suspension polymerization, these are designated as primary aggregates of PVC chains). The primary aggregates of PVC chains are unstable and aggregate to form primary particles. Because the concentration of the protective colloid is low and its ability to stabilize primary particles is limited, most primary particles will further aggregate to form grains. Therefore, the polymerization is carried out in a VCM/*n*-butane mixed medium (the composition of the mixture will change continuously as the polymerization proceeds) and gives particles with different sizes (i.e., primary aggregates of PVC chains, primary particles, and grains). Primary particles and grains grow by the capture of newly formed PVC chains and their primary aggregates, and polymerization occurs inside them. Primary aggregates of PVC chains, primary particles, and grains coexist during the polymerization process and also in the PVC resin.

The particle features of PVC resins prepared by the new polymerization process can be explained by the aforementioned particle formation mechanism. Because the primary aggregates of PVC chains and primary particles are very small, their existence in the resulting PVC resin leads to a decrease in  $D_n$  of the resin. PVC grains are formed by the direct aggregation of primary particles in the agitated medium, so their shapes are more regular and their surfaces are smoother than those of the suspension PVC resin. The PVC grain/reaction medium interface is always changing as more and more primary particles are captured by the grain, so no obvious skin will be formed at the surface of PVC grains. The solubility parameter difference between PVC and the VCM/*n*-butane mixture is great and increases with increasing conversion. Also, the swelling capacity of the VCM/*n*-butane mixture in PVC is very low, and the glass-transition temperature of PVC is greater than the polymerization temperature, so PVC primary particles do not adhere enough to fuse during the polymerization process. As a result, PVC grains with looser aggregates of primary particles and high porosity are formed. The absence of a skin and the formation of looser aggregates of primary particles lead to the separation of some primary particles from the grains in the subsequent handling of the PVC resin (and in particle size measurements), but this favors the removal of the unreacted monomer and the processing of the PVC resin. Primary particles in the top layer of the PVC grains are always formed later and have a shorter residence time in the reactor, so they are smaller than the primary particles in the center part of the grain. Also, PVC grains with higher conversions have larger primary particles in their centers, as evidenced by the SEM micrographs.

## CONCLUSIONS

PVC resins with a particle morphology quite different from that of a suspension PVC resin were prepared by a new heterogeneous polymerization process, with *n*-butane as the reaction medium. The resulting PVC resins exhibited a regular particle shape, smooth particle surfaces with no obvious skin, looser aggregation of primary particles, and a high porosity compared with those of the suspension PVC resin. In view of the particle features of the resulting PVC resins, the particle formation mechanism of the new polymerization process was proposed as follows: PVC chains precipitate from a VCM/*n*-butane mixed medium to form primary aggregates at a very low polymerization conversion, and primary aggregates of PVC chains aggregate to form the primary particles, which further aggregate to form the grains. The primary particles and grains grow by the capture of newly formed PVC chains and their primary aggregates and by the polymerization occurring inside the aggregates.

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