Experimental Investigation of Vinyl Chloride Drop Behavior During Suspension Polymerization

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ABSTRACT: The effects of some polymerization conditions on poly(vinyl chloride)(PVC) particles produced by the suspension polymerization process were studied on a laboratory scale. The different stages of vinyl chloride suspension polymerization were investigated experimentally by using an on-line sample withdrawal technique during reaction. It was found that the method of addition of initiator has a great effect on the PVC particle uniformity as well as the size distribution. Furthermore, when the initiator was predispersed in the continuous phase, some latex particles were formed. The effect of the type of stabilizer was also studied with two different types of PVA [partially hydrolyzed poly(vinyl acetate)]. It was found that by changing the stabilizer, the particle size, the porosity, and the morphology could change. When H80 (PVA with a degree of hydrolysis of 80% and a molecular weight of 259,000) stabilizer was used, the rigidity of the PVC particles was weak. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 127–134, 1997

Key words: suspension polymerization; vinyl chloride; particle size; morphology; stabilizer

INTRODUCTION

Because of the insolubility of the polymer in its monomer, the polymerization of vinyl chloride monomer (VCM) is a heterogeneous process. It involves several physical transitions throughout the course of the polymerization. In suspension polymerization, each droplet behaves as a mini-bulk reactor. During the initial stages, small entities known as primary particles are formed inside the droplets. Their growth and subsequent aggregation mechanisms are responsible for the internal morphology of the final particles. Because of the carcinogenic aspect of the VCM, scientists have been looking for ways of decreasing the free monomer content in the poly(vinyl chloride) (PVC) particles. The straightforward method is

to increase the porosity of the particles, thus controlling their morphology.

The general mechanism of polymer formation in the vinyl chloride droplet during suspension polymerization can be divided into three main stages.[1–3] In the first stage, which takes place between 0 and 0.1% conversion, the reaction (inside the vinyl chloride droplet) is considered to be a homogeneous polymerization process because the polymerization occurs only in the monomer phase.[4] In the second stage, which lasts up to 70% conversion, heterogeneous polymerization takes place. Throughout this stage, there exist two phases in which polymerization occurs simultaneously—a monomer-swollen polymer phase and a relatively pure monomer phase. Stage three starts at 70% conversion, when the monomer-rich phase is exhausted. The process is again considered homogeneous because the polymerization occurs only in the monomer-swollen polymer phase. In order to control the morphology of the final
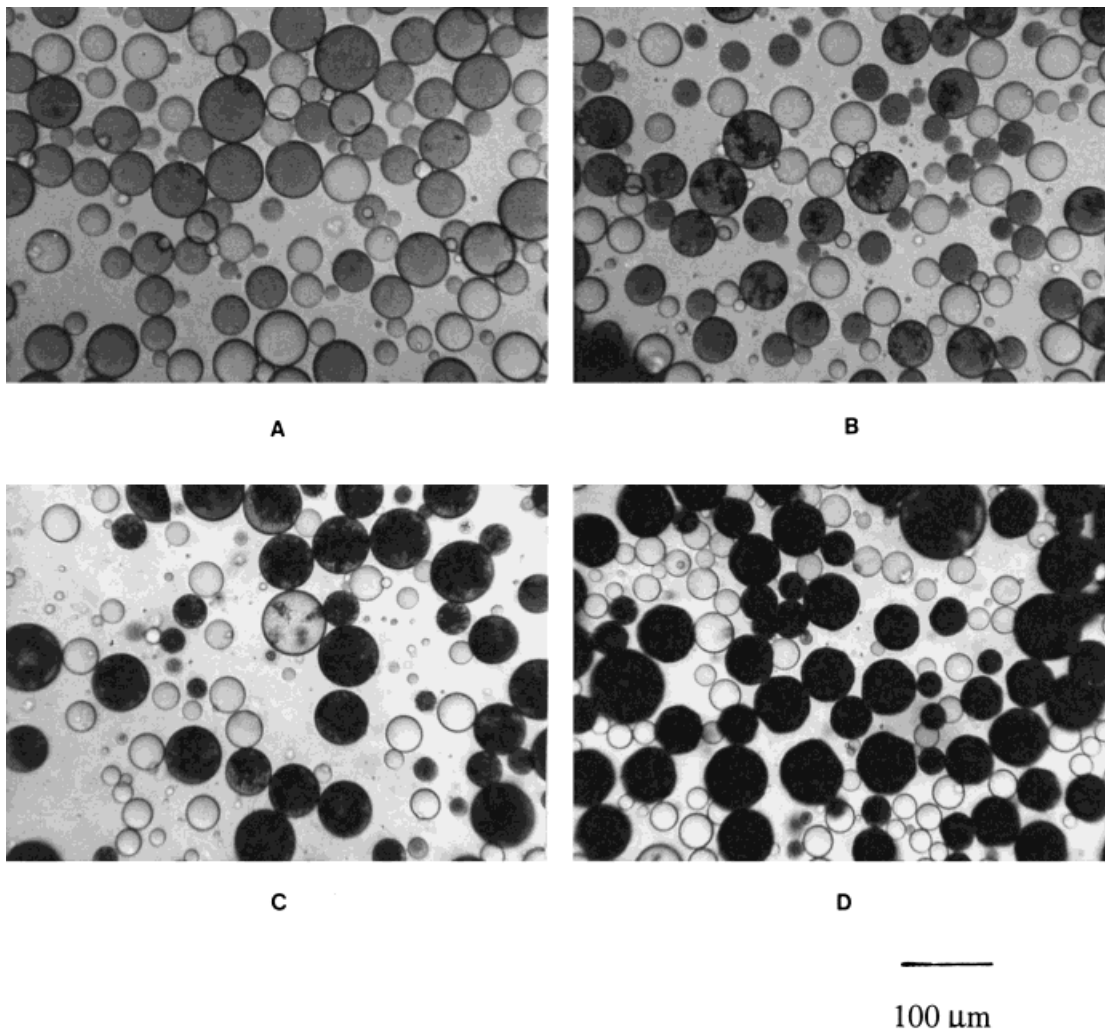
Figure 1   Changes occurring in vinyl chloride droplets during early stages of suspension polymerization ($\varphi = 0.1$, $N = 350$ rpm, X50 concentration = 0.175%, PVA concentration = 0.06%, and $T = 55°C$). (A) 5 min, (B) 10 min, (C) 20 min, (D) 60 min.

PVC particles, it is necessary to understand the different stages of the vinyl chloride suspension polymerization process as well as the parameters that can affect them. The object of this work is to study experimentally some aspects of droplet formation and subsequent droplet agglomeration for different experimental conditions during the vinyl chloride suspension polymerization process.

EXPERIMENTAL

The apparatus used in this work consisted of a stainless steel jacketed reaction vessel of 1-L capacity fitted with four equally spaced stainless steel baffles, each $\frac{1}{10}$ the tank diameter. The agita-

tor was a six-flat-blade turbine. The reaction vessel was connected externally to a pressurized stainless steel optical cell mounted on an optical microscope for sample withdrawal and photography.

The reaction mixture used for these experiments consisted of liquid VCM (supplied by EVC, UK Ltd) as the dispersed phase and distilled water as the continuous phase. The reactor pressure was 10 bar. Two types of suspending agents, partially hydrolyzed poly(vinyl acetate)(PVA), were used: H72, which has a degree of hydrolysis of 72.5% and a molecular weight of 75,000, and H80, which has a degree of hydrolysis of 80% and a molecular weight of 259,000. The initiator used was *bis*(4-*t*-butylcyclohexyl)peroxydicarbonate (X50). Details of the design and operation of the
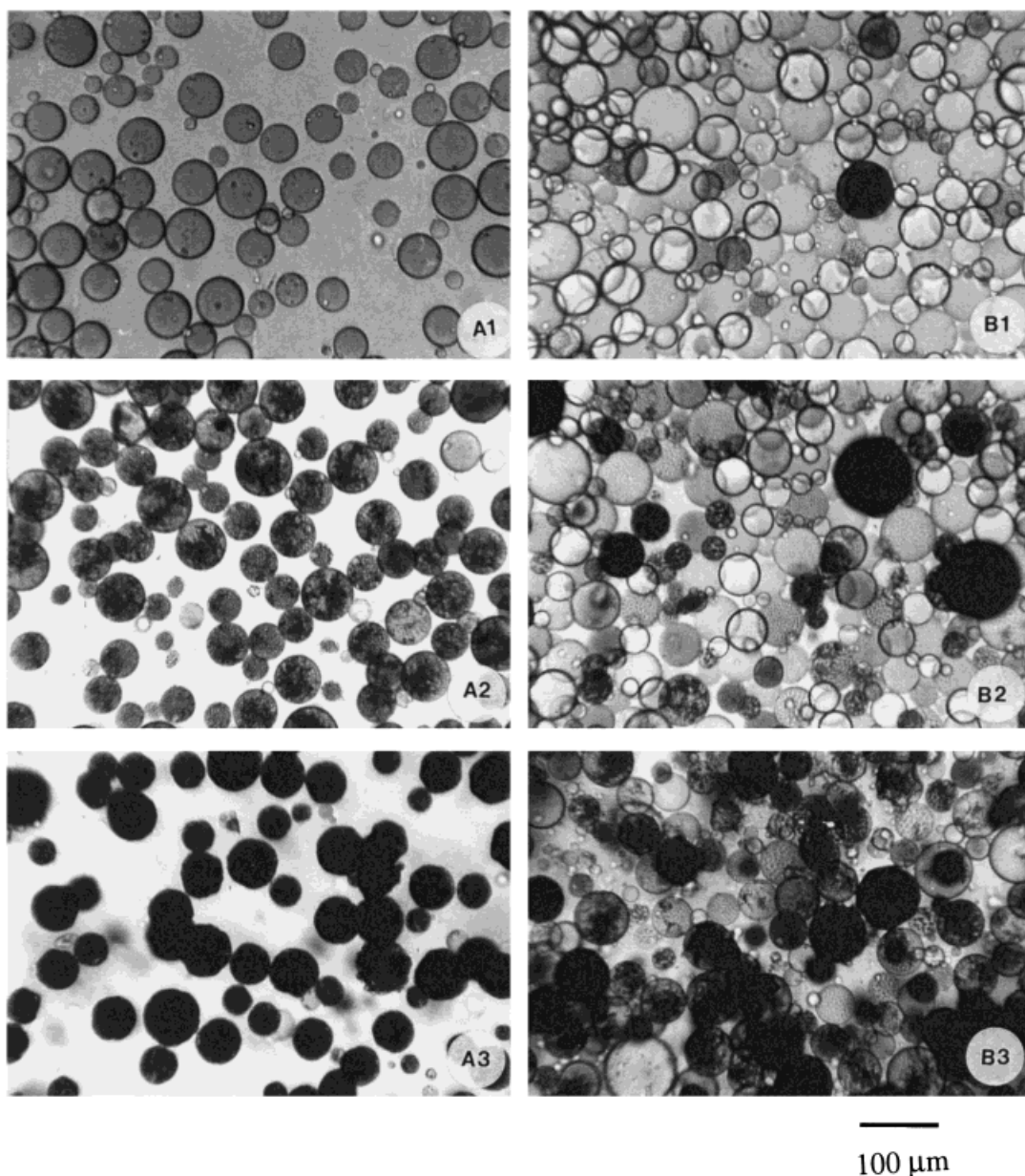
Figure 2   Effect of the method of addition of initiator on the uniformity of the vinyl chloride droplets during suspension polymerization ($\varphi = 0.1$, $N = 350$ rpm, X50 concentration = 0.175%, PVA concentration = 0.06%, and $T = 55°C$). (A) Initiator predissolved in VCM, (A1) 5 min, (A2) 20 min, (A3) 60 min. (B) Initiator dispersed in the continuous phase, (B1) 5 min, (B2) 20 min, (B3) 60 min.

apparatus and of the experimental procedure are described elsewhere.[5,6] For all of the polymerization experiments performed, the reaction temperature was 55°C while the agitator speed was 350 rpm. The initiator concentration was 0.175% (Wt_{X50}/Wt_{VCM}). The volume fraction of the dispersed phase was 0.1, and the suspending agent concentration (PVA) was 0.06% (Wt_{PVA}/Wt_{water}).

RESULTS AND DISCUSSION

Effect of Polymerization Conditions on the Vinyl Chloride Droplet Morphology and Uniformity

The aim of this series of experiments is to show the different stages of VCM suspension polymerization as well as to study the effect of the method

Table I   Variation of Conversion Versus Polymerization Time

Polymerization Time (min)	Conversion (%) (for X50 Predissolved in VCM)	Conversion (%) (for X50 Predispersed in Continuous Phase)
5	<1	<1
10	2.8	2
20	7.5	4.5
60	26.9	20.6
120	61	54

of addition of initiator on the morphology and uniformity of the polymerizing vinyl chloride droplets. In these experiments, H72 was used as a suspending agent. In each experiment, samples were forced into the pressurized optical cell and photographs were taken at different stages of the polymerization. Figure 1 shows vinyl chloride suspension polymerization at the early stages of the reaction. In the latter experiment, the initiator was predispersed in the continuous phase (this method of addition of initiator is used in the industrial manufacture of suspension PVC) and a certain amount of reflux was occurring through the lid of the reactor (the lid was not heated). It can be seen from the four photographs that the droplets are not uniform because some polymerized while others did not. Photograph A (<1% conversion) shows the stable and uniform primary particles formed, after a reaction time of 5 min, in the VCM droplets in which polymerization has started. These growing primary particles are thought to be stabilized by electrostatic forces due to the presence of chloride ions.[7,8] These negative charges are evenly adsorbed at the polymer/monomer interface. Photograph B ($\approx$ 2% conversion) shows the second stage of the polymerization, when the primary particles reached a critical size above which the stability due to electrostatic forces is inhibited and the primary particles (or agglomerates at this stage) coagulate to form a "cloud." Photograph C ($\approx$ 4.5% conversion) shows that most of the primary particles have coagulated and formed a more or less continuous "cloud" inside the droplet. After 60 min ($\approx$20.6% conversion; photograph D), a close packing within the droplets is formed. The shape of the final PVC particle is defined at this stage (if enough stabilizer is used to protect the drops). This mechanism is similar to the one proposed by Smallwood.[9] In order to study the effect of the

method of addition of initiator on the polymerizing VCM droplets, two experiments were performed using the same experimental conditions as the latter ones, except that the reactor's lid was heated to avoid reflux. In the first experiment, the initiator was predissolved in the VCM and then poured into the continuous phase for mixing and polymerization. In the second experiment, the initiator was first predispersed in the continuous phase and then the monomer was added into the reaction mixture. For each experiment, samples were forced into the optical cell at different reaction times (5, 20 and 60 min, respectively) and photographed. The results obtained are shown in Figure 2. The photographs presented in Figure 2 represent samples of vinyl chloride droplets during suspension polymerization at different reaction times for both methods of addition of initiator. Table I shows the variation of conversion with polymerization time for both cases. We can see from the latter figure that when the initiator is predissolved in the VCM, the polymerization occurs uniformly in all of the droplets, while if the initiator is just dispersed in the continuous phase, the polymerization does not occur uniformly inside the droplets. These results show that the diffusion of initiator from the continuous phase into the VCM droplets is not instantaneous. They also show that the coalescence rate between the droplets is relatively low at the early stages of the polymerization because the initiator is not spreading rapidly between the VCM droplets. The effect of the method of addition of initiator on the PVC particle size distribution is shown in Figure 3. The size distributions shown in Figure 3 were taken for PVC particles which were polymerized for 60 min, and then, the reaction was stopped and the PVC particles were filtered and dried. A sample of PVC particles was ultrasonically dispersed in distilled water (wetting of the PVC particles was improved by adding a proprietary surfactant type Brij-35) and analyzed with a Coulter LS130 laser sizer. When the initiator was dispersed in the continuous phase, a certain amount of latex particles (particles of a size <2 μm) was observed in the final product [see Fig. 3(A)]. This confirms that emulsion polymerization is also taking place. This might be because, when the VCM diffuses into the continuous phase (although in very small quantities), it polymerizes using the free dispersed initiator which did not move into the VCM droplets forming latex particles. When the initiator was predissolved in the VCM prior to polymerization, the particle size distribution does not show any latex formation [see Fig. 3(B)]. It also shows the
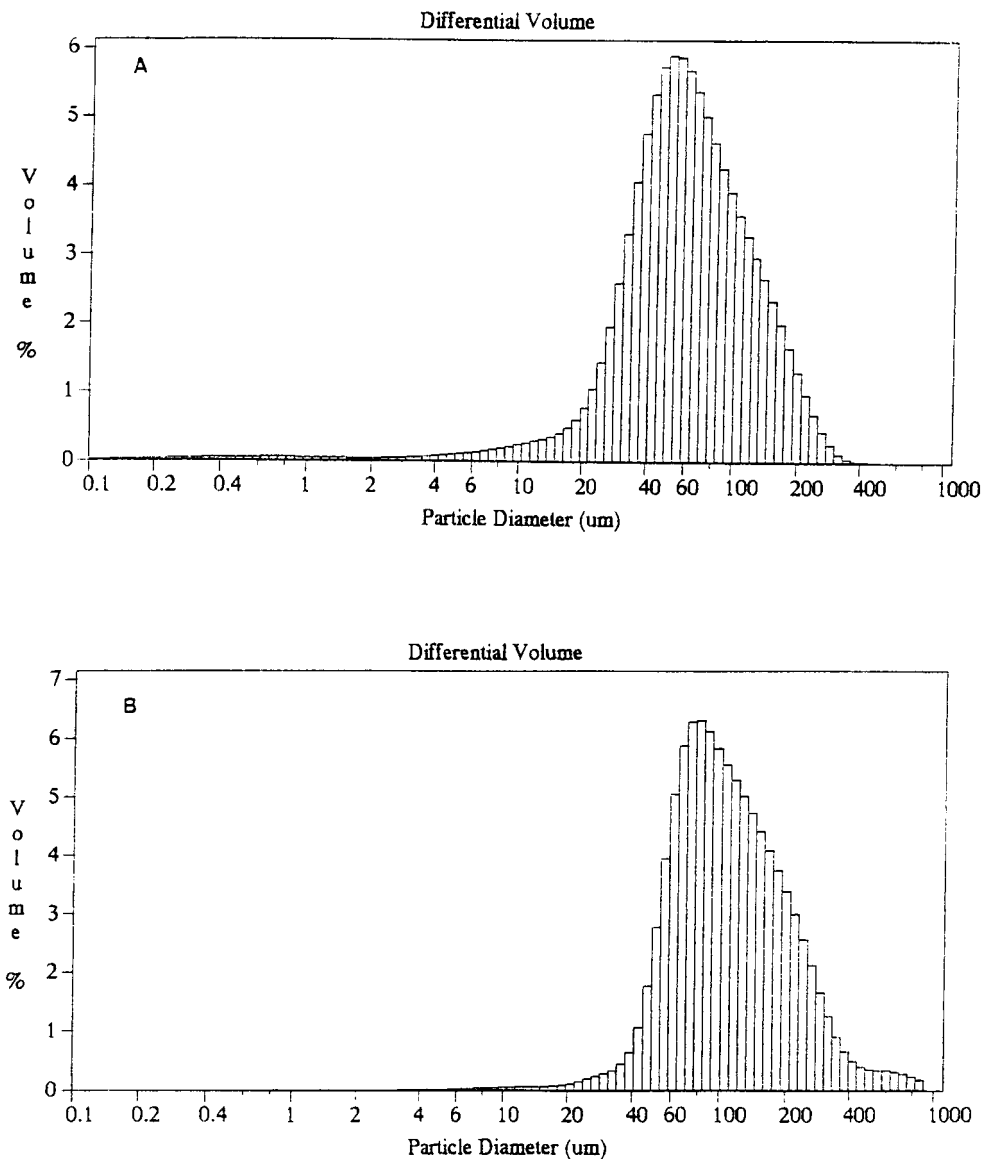
Figure 3 Suspension PVC particle size distribution (reaction time, 60 min; PVA concentration = 0.06%; X50 concentration = 0.175%; $T = 55°C$; and $N = 350$ rpm) for (A) initiator (X50) predispersed in the continuous phase, (B) initiator (X50) predissolved in the VCM phase.

existence of few large PVC particles, probably formed by the coalescence of smaller ones when the reaction was stopped. Thus, the method of addition of initiator plays an important role in determining the degree of uniformity of the final PVC particles (i.e., size, size distribution, porosity, and degree of conversion[10]).

Polymerization Experiments with H80 as Stabilizer

The influence of the type of suspending agent was studied with the H80 suspending agent instead of H72. The experimental procedure was the same

as above except that the initiator (X50 solid) was predissolved in VCM. The concentration of stabilizer (H80) used was 0.06% (Wt_{H80}/Wt_{water}). The suspension polymerization reaction was run for 180 min, and samples were withdrawn into the optical cell and photographed at different time intervals. Figure 4 shows the drop behavior at the different stages of the vinyl chloride suspension polymerization. From Figure 4, we observe that the droplets are bigger and more uniform in size than when the H72 stabilizer is used. The morphology seems to be similar to the droplets produced using H72 stabilizer up to a reaction time
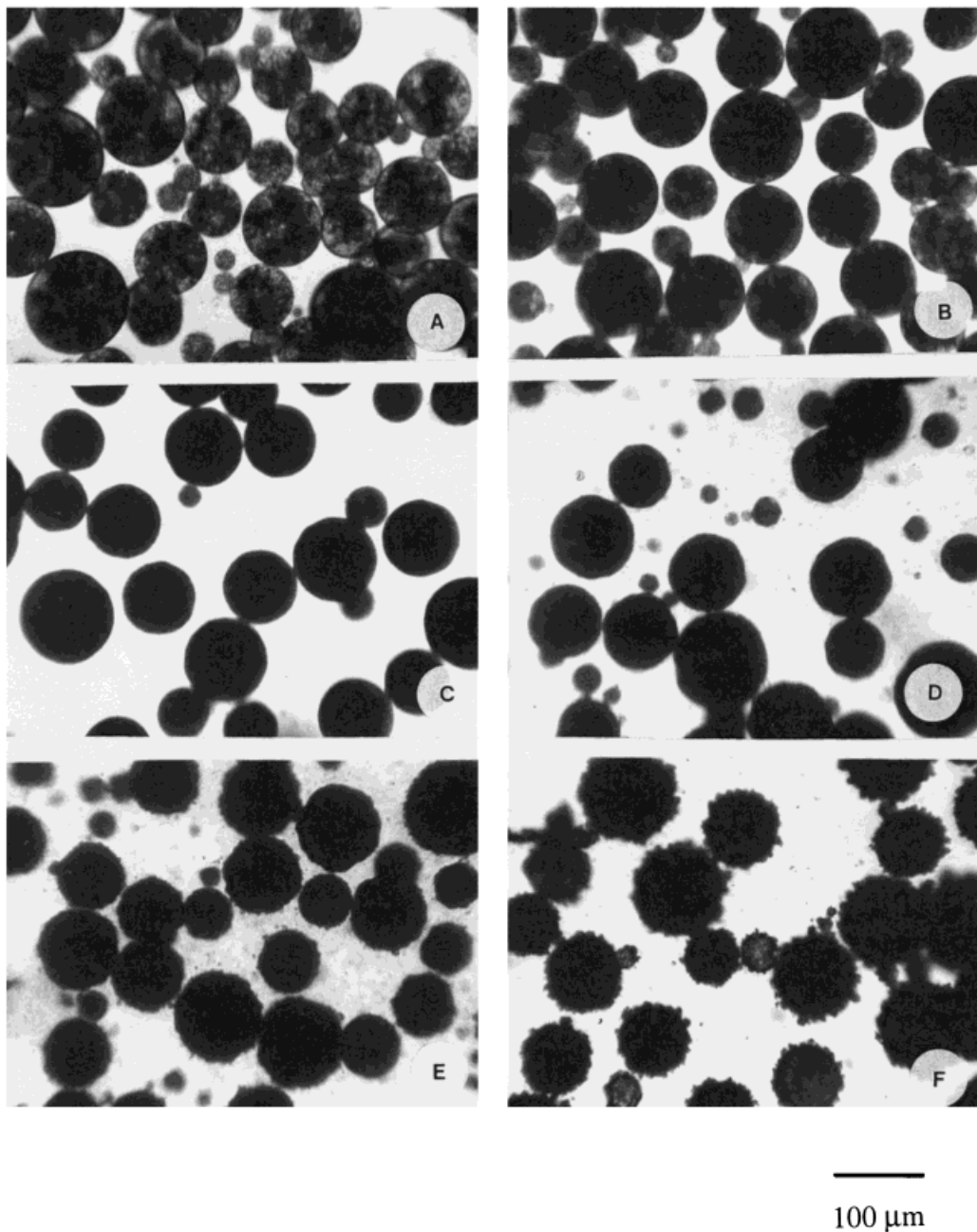
100 μm

Figure 4   Changes occurring in vinyl chloride droplets during different stages of suspension polymerization with H80 as stabilizer (X50 predissolved in the VCM with no reflux occurring). (A) 15 min, (B) 30 min, (C) 45 min, (D) 60 min, (E) 90 min, (F) 120 min.

of 90 min; then, the PVC particles start losing their smooth spherical shape and begin adhering to each other. The analysis of the final PVC particles by a scanning electron microscopy technique is shown in Figure 5, which shows an agglomeration of PVC particles (photograph A) and a view of the surface of one of the particles (photograph B). The surface looks very rough, which shows

that H80 might be a good stabilizer at the early stages of the polymerization; however, once, the PVC particles are formed, the thin "skin" at the surface of the particle is not rigid enough to preserve its shape beyond a certain conversion stage. When H72 is used as the stabilizer, the surface of the final particles is smooth (see Zerfa and Brooks[10]). The porosity of the final PVC particles
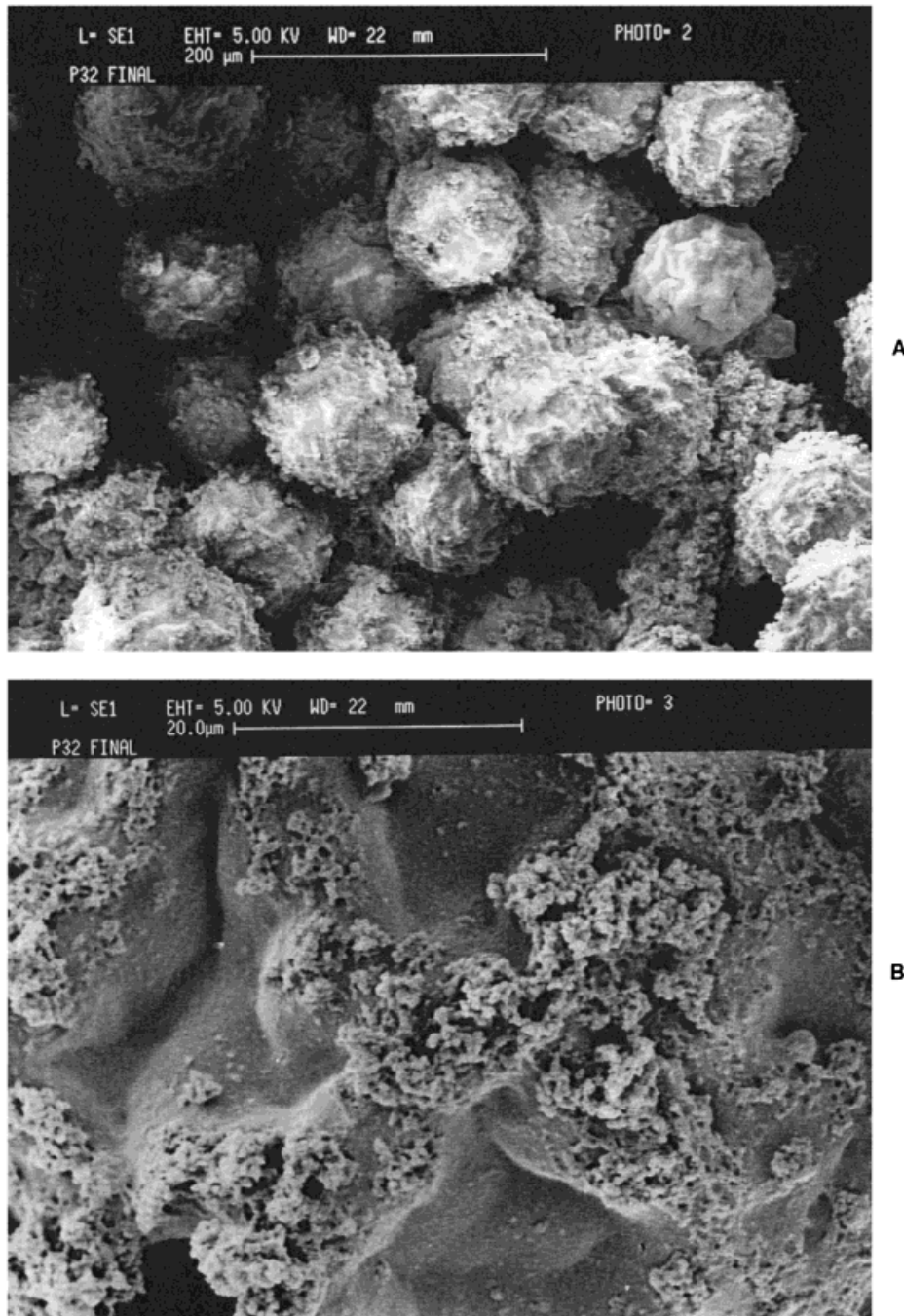
Figure 5 Scanning electron microscopy photographs of suspension PVC particles stabilized with H80 (X50 predissolved in VCM). (a) PVC particles, (b) scanning of a surface of a PVC particle.

was relatively low (using the cold plasticizer technique, the porosity was equal to 14.05% for a polymerization conversion of 80%, compared with a porosity of $\approx$ 24% when H72 is used as the stabilizer). When the initiator was predispersed in the continuous phase, the porosity of the final PVC grains decreased to 8.45% (with H80 as the stabi-

lizer) and the conversion was 65%. When H72 was used as the stabilizer, the porosity was $\approx$ 33% for the same conversion. Thus, the H80 stabilizer enhances the uniformity of the initial VCM droplets while H72 provides the rigidity needed for the outside skin as well as for conserving the final shape of the PVC particles.

CONCLUSIONS

This work was devoted to the study of the effect of some influential parameters of the suspension polymerization of vinyl chloride. The main conclusions are as follows:

- When the initiator is predispersed in the continuous phase, the polymerizing VCM droplets are not uniform and a parallel emulsion polymerization process may occur.

- The method of addition of initiator has a great effect on the particle size distribution of the final PVC particles.

- When the initiator is predispersed in the continuous phase, its diffusion to the VCM droplets is slow.

- The type of stabilizer can affect the PVC particle's shape, size distribution, and porosity.

- When H80 is used as the stabilizer, the surface of the polymerizing VCM droplets loses its smoothness.

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