Drop Coalescence Processes in Suspension Polymerization of Vinyl Chloride

M. ZERFA and B. W. BROOKS*

Department of Chemical Engineering, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, United Kingdom

SYNOPSIS

A tracer dye technique was used to investigate the effect of turbulence intensity, stirring time, and the type and concentration of the suspending agent, partially hydrolyzed poly(vinyl acetate) (PVA), on the coalescence rate of vinyl chloride monomer (VCM) droplets in an agitated liquid–liquid dispersion. It was found that the extent of coalescence rises slowly with mixing time, is roughly proportional to the agitation speed, and decreases sharply when the concentration of stabilizer is increased. Coalescence rate depended on the degree of hydrolysis of the stabilizer. The method of addition of initiator during VC suspension polymerization was also studied and its effects on the polymerization conversion and final PVC particles' properties were determined. It was found that the polymerization reaction occurs more uniformly in all the VCM droplets when the initiator was predissolved in the VCM prior to reaction compared with the case when the initiator was predispersed in the continuous water phase. Also, for the same reaction time, the conversion was higher in the former case. During polymerization, the concentration of PVA in the aqueous phase decreased substantially and the porosity of the polymer particles was reduced. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The drop size and size distribution of dispersed phase droplets in a liquid–liquid dispersion are mainly determined by the rates of breakage and coalescence. The former rate produces smaller droplets while the latter forms larger drops, hence, causing mixing within the dispersed phase. Thus, characterizing these processes would help solve problems involving mass transfer and chemical reaction as in the case of suspension polymerization. In trying to understand the effect of experimental conditions on coalescence rate, a variety of experimental approaches were used in the past. Among these experimental methods the spread of a tracer dye between drops was the most popular.[1-6] Most of the workers limited their studies to the determination of the average coalescence frequencies. This physical method is based on the measurement of dye (soluble

only in the dispersed phase) dispersion in the dispersed phase using either light transmittance or photographic means. Direct determination of coalescence frequencies in a turbulent liquid–liquid system is very difficult. To directly observe and measure the drop coalescence frequencies in an agitated vessel, Park and Blair[7] used high speed cinematography. The results obtained from this method are not very reliable as very few coalescences are observed compared with the total number of coalescences occurring, hence, the problem of statistical representation occurs.

The product quality of suspension poly(vinyl chloride) (PVC) is to a large extent controlled by the particular suspension stabilizer as well as the way the polymerization process is conducted. Although a great deal of work has been devoted to the stabilized droplets, there is very little literature related to the effect of stabilizer on the PVC particle. The few studies related to this subject and reported in the literature have shown that the porosity of a PVC resin is strongly affected by the surface activity of the stabilizer,[8-13] but, the mechanism by which
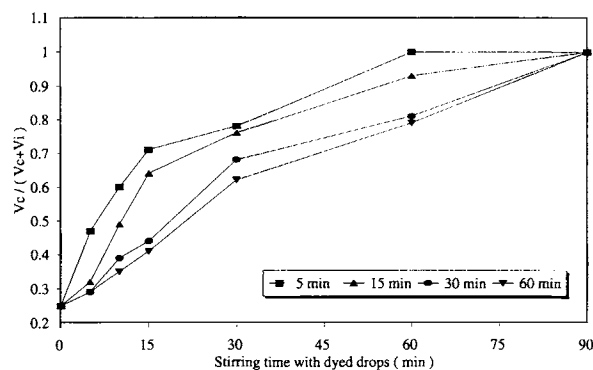

Figure 1 Variation of $V_c/(V_c + V_i)$ with stirring time at different premixing time of the nondyed droplets. (C_{PVA} (72.5% hydrolysis) = 0.02%; N = 500 rpm.

the suspension stabilizers exert their influence is still mainly unknown. The PVC grain size is usually assumed to be controlled by the suspension stabilizing system and the intensity of agitation.[14-16] When the experimental conditions were "critical" (i.e., insufficient stabilizer or a relatively high turbulence), the surface of the PVC grain was found to have an irregular appearance on the surface and a nonuniform size. Nilsson et al.,[16] in studying drop and grain size distribution during suspension polymerization of vinyl chloride monomer (VCM), found that the average PVC grain volume at 5% conversion was five times larger than the average monomer volume. They also found that there was no change in grain size between 5% and full conversion.

It is well known that initiators of polymerization in PVC manufacture are usually azo or peroxide compounds that are soluble in the VCM. These initiators are assumed to be homogeneously distributed between the VCM droplets by the time polymerization starts. This could be the case when the initiator
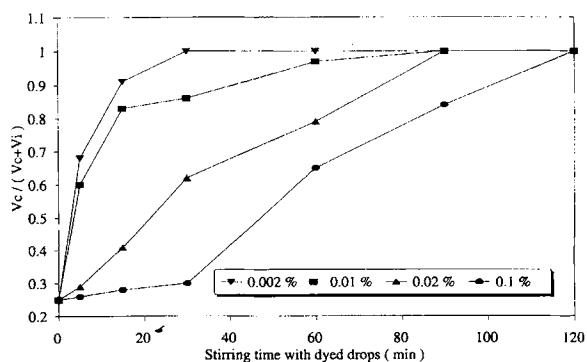

Figure 2 Variation of $V_c/(V_c + V_i)$ with stirring time at different PVA concentrations (72.5% hydrolysis. N = 500 rpm, premixing time 30 min.
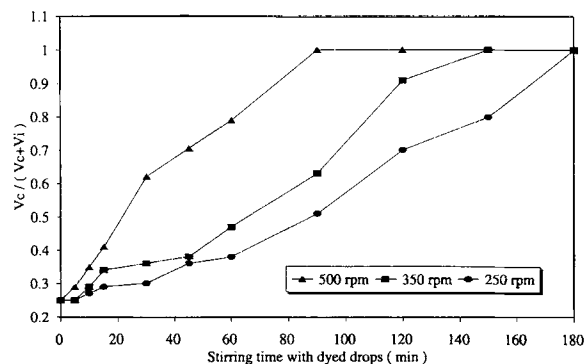

Figure 3 Variation of $V_c/(V_c + V_i)$ with stirring time at different agitator speeds. C_{PVA} (72.5% hydrolysis) = 0.02%, premixing time 30 min.

is predissolved in the monomer prior to the start of the polymerization reaction. However, if the initiator is predispersed in the continuous aqueous phase (for safety reasons in industrial production), the latter assumption may not be correct.

In the present study, an experimental method was used to demonstrate the relative effect of some experimental conditions on the rate of coalescence of the VC droplets and to investigate the effect of the method of addition of initiator on the PVC particles. This is important when initiator is to be added to preformed drops.

EXPERIMENTAL

The liquid–liquid system used for the experiments consisted of VCM (supplied by EVC, UK Ltd.) as the dispersed phase and distilled water as the continuous phase. The suspending agent, partially hydrolyzed poly(vinyl acetate) (PVA), was either H72 (degree of hydrolysis of 72.5%) or H80 (degree of hydrolysis of 80%). The dye used for the coalescence studies was Sudan red B (organic dye) supplied by Aldrich. During the suspension polymerization, the initiator used was bis(4-t-butylcyclohexyl)peroxydicarbonate.

The apparatus consisted of a stainless steel jacketed vessel (capacity 1.0 L) fitted with four equally spaced stainless steel baffles, each $\frac{1}{10}$ of the tank diameter. The agitator was a six blade flat turbine. The mixing vessel was connected externally to a pressurized stainless steel optical cell for sample withdrawal and photography. Details of the design and operation of this apparatus and of the experimental procedure (sampling and PVA concentration measurements) are described elsewhere.[17,18]
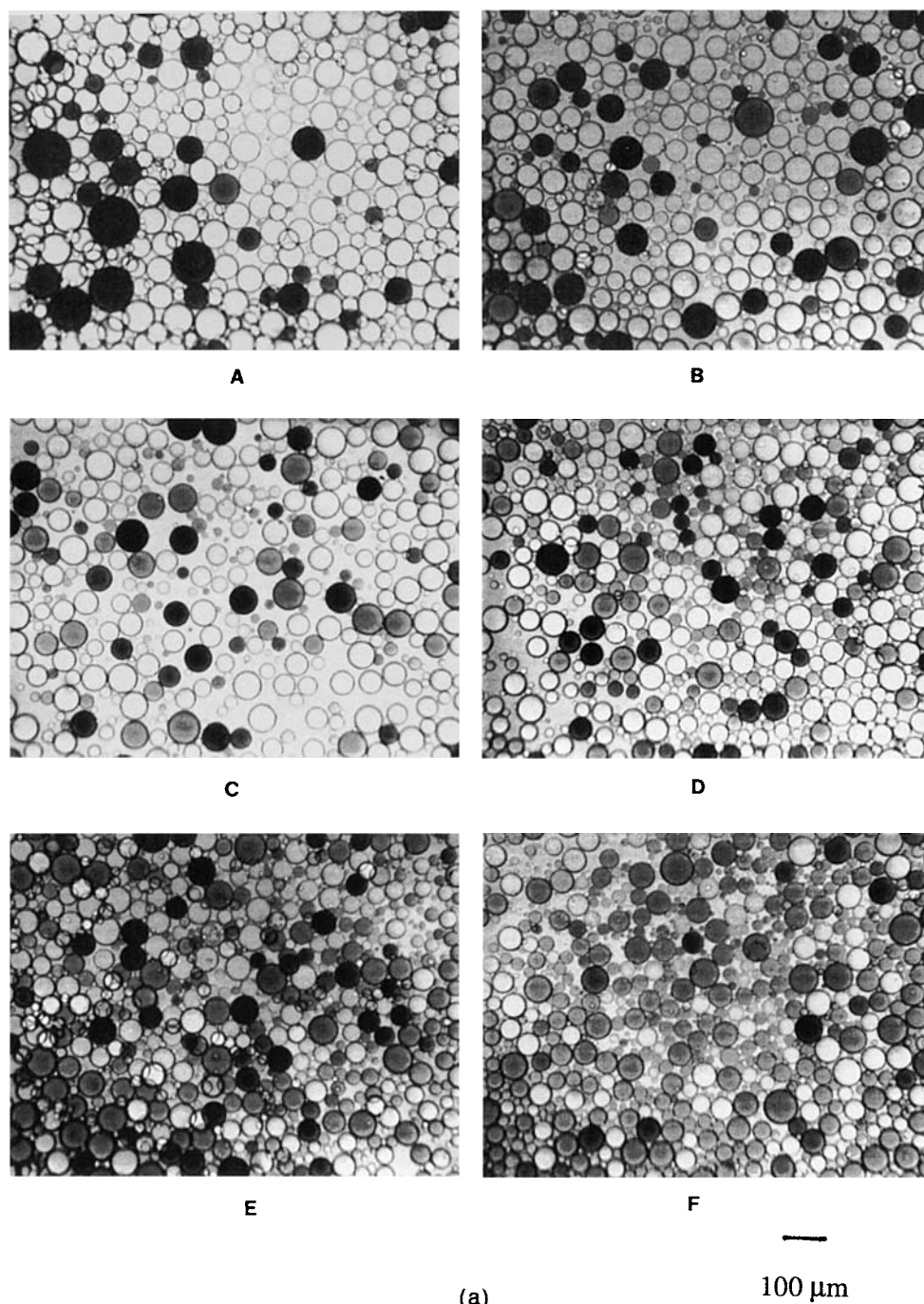
(a)   100 μm

Figure 4 Dyed vinyl chloride droplets added to preformed suspensions at different stirring times of dyed VCM, stabilized using (a) PVA (H72), with N = 250 rpm and C_{PVA} = 0.02%, and (b) PVA (H78), with N = 350 rpm and C_{PVA} = 0.02%: (A) 5 min, (B) 15 min, (C) 45 min, (D) 60 min, (E) 90 min, and (F) 150 min.

Effect of Mixing Conditions on Coalescence Rate Between VC Droplets

The aim of this series of experiments was to study the effect of experimental conditions on the co- alescence rate. For this purpose, three parameters believed to have a great influence on the coales- cence rate were investigated: the stirring time, the suspending agent concentration, and the turbu- lence intensity (agitation speed). SUDAN red "B"
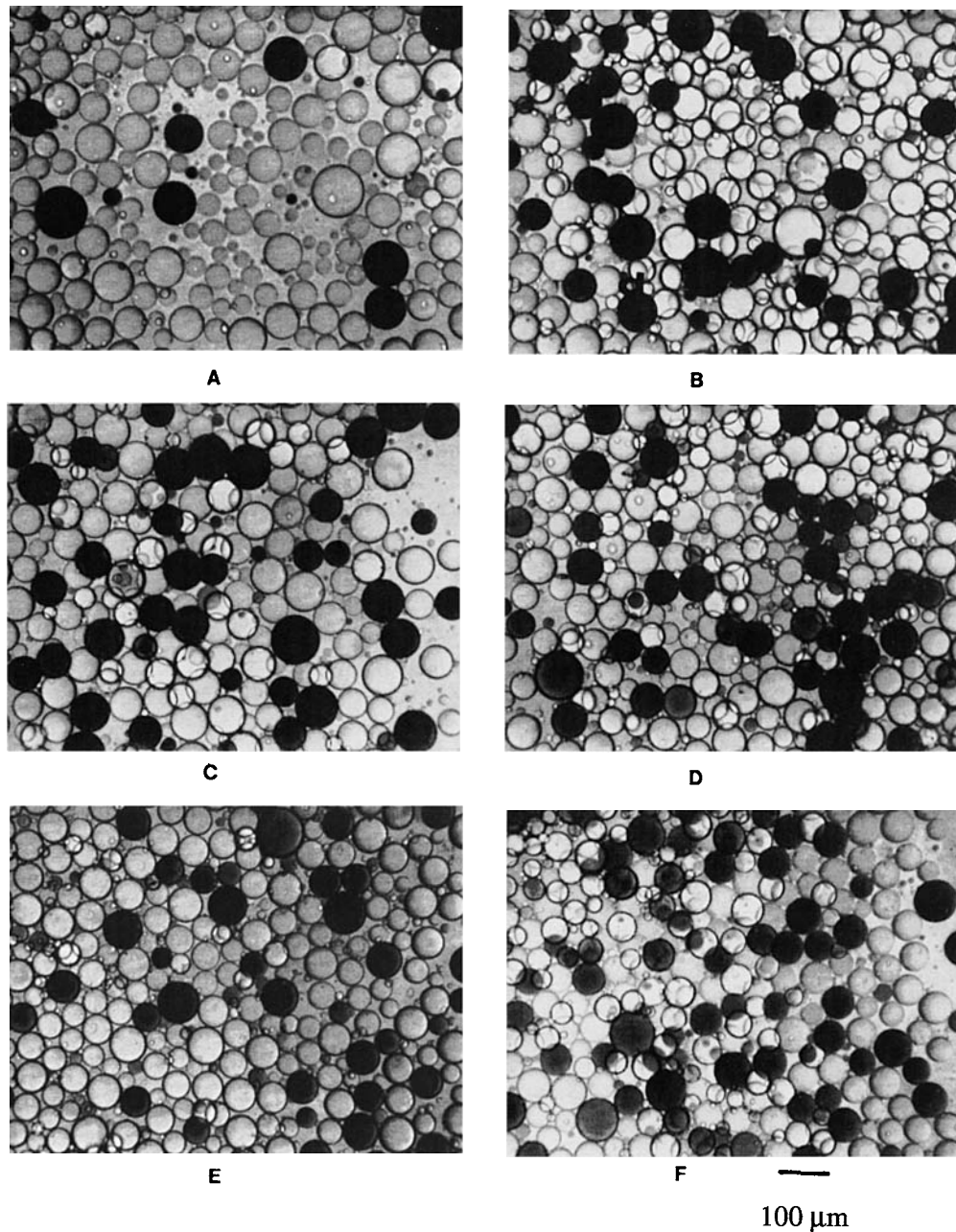
A

B

C

D

E

F

100 μm

Figure 4 (*Continued from the previous page*)

dye (0.1 g) was put into a small stainless steel cylinder (150-mL capacity). This was then purged with nitrogen to remove the air before the addition of 25 g VC. The mixture was then shaken to accelerate the dissolution of the dye. The cylinder was then fixed onto the top of the reactor's lid and connected to a nitrogen cylinder. The continuous phase [0.9 L of distilled water containing the suspending agent (H72 or H80)] was charged into the reactor tank, which was then sealed and deoxygenated. Seventy-five grams of fresh VC was then forced into the reactor tank and stirred at the required agitation speed. The tank was then heated to 55°C. At a later stage, the dyed VCM was added into the reaction mixture and samples were photographed at regular intervals and analyzed for coalescence rate. To differentiate between dyed and nondyed droplets, a filter (filter type tricolor green) was used for the microscope light, which gives a darker color for the dyed VCM droplets. This procedure was used throughout this series of experiments.
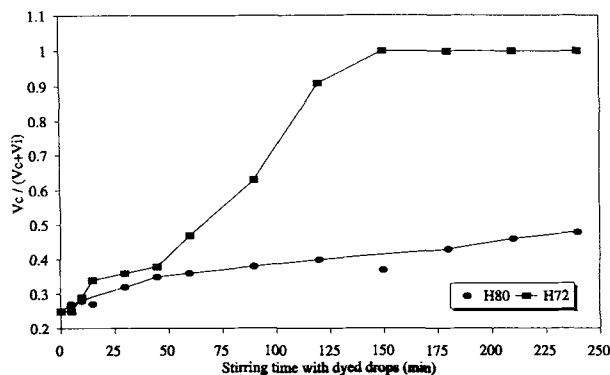
Figure 5 Variation of $V_c/(V_c + V_i)$ with stirring time of dyed VCM droplets for H80 and H72 stabilizers. N = 350 rpm, C_{PVA} = 0.02%.

Effect of Method of Addition of Initiator on Conversion and PVA Adsorption

The aim of this series of polymerization experiments was to investigate both the effect of the method of addition of initiator on conversion and the PVA adsorption rate as a function of conversion. For this purpose, the following experimental procedure was used. A specific amount of PVA (type H72, 72.5% degree of hydrolysis) was predissolved in 1 L distilled water (about 0.06, wt_{PVA}/wt_{WATER}) that was then poured into the reactor. The continuous aqueous phase was maintained at about 15°C using cooling water (through the reactor jacket). Then 0.7 g initiator in suspension (0.175%, $wt_{INITIATOR}/wt_{VCM}$) was added into the continuous phase and stirred. The reactor was then sealed and deaerated using nitrogen. One hundred grams of VCM was then forced into the reactor and the agitator run at 350 rpm. The reaction mixture was then heated to 55°C. In a series of separate experiments, reactions were run for 15, 30, 45, 60, 90, 120, 150, 200, 250, and 300 min, respectively.

Because the VC polymerization reaction is exothermic, the reaction temperature was controlled by regularly adding some ice into the water bath used to cool the reactor. For each experiment, samples were forced into the pressurized optical cell and photographs were taken at different stages of the polymerization. At the end of each polymerization reaction, the stirrer was stopped for about 4 min (to allow the droplets to separate from the continuous phase) and a sample of the continuous phase was taken from the bottom of the reactor to be analyzed for PVA concentration. The stirrer was then run at 350 rpm with no heating so that unreacted VC slowly vented through the extractor via the venting valve. Once the venting was completed, the reactor's con-
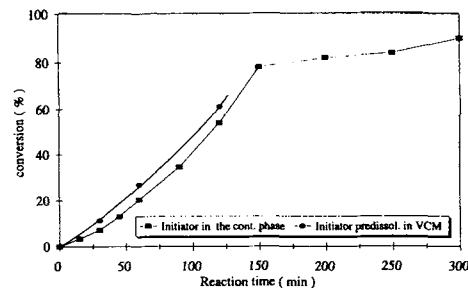
tents were heated to 80°C to remove the residual VCM (about 1,000 ppm). The reactor was then cooled down and the contents removed into a glass flask. The PVC product was filtered, dried, and weighed. The same procedure was used for the second set of experiments except that the initiator (in a solid powder form) was predissolved in the VCM prior to the polymerization reaction.

RESULTS AND DISCUSSION

Effect of Mixing Conditions on Coalescence Rate Between VC Droplets

The first parameter to be studied in this series of experiments was the stirring time of the noncolored droplets (premixing time t_i) in the presence of stabilizer. The aim was to determine the necessary stirring time for the noncolored droplets to become relatively stable toward coalescence. The concentration of suspending agent used (H72, degree of hydrolysis 72.5%) was 0.02% and the agitator speed

Figure 6 Variation of vinyl chloride monomer suspension polymerization conversion with reaction time. C_{PVA} (72.5% hydrolysis) = 0.06%, initiator concentration = 0.175%, and N = 350 rpm.

Table I Percentile Particle Sizes (μm) by Cumulative Volume for Different Conversions

Conversion (%)	Cumulative Volume				
	10	25	50	75	90
3.4	8.153	24.63	48.77	78.63	113.8
7.2	25.38	40.56	62.33	89.73	121.5
13	29.96	44.79	67.71	105.2	153.1
20.8	33.34	51.64	83.34	135.8	199.7
34.5	60.41	95.49	160.1	247.1	330.5
54	58.05	115.6	252.8	420.3	605.7
90	127.7	241.7	354.2	458.9	554.6

Monomer volume fraction = 0.1; N = 350 rpm; C_{PVA} (72.5% hydrolysis) = 0.06%; initiator concentration = 0.0175%.

PVC particle size distribution at 3.4 % polymerisation conversion.

PVC particle size distribution at 34 % polymerisation conversion.

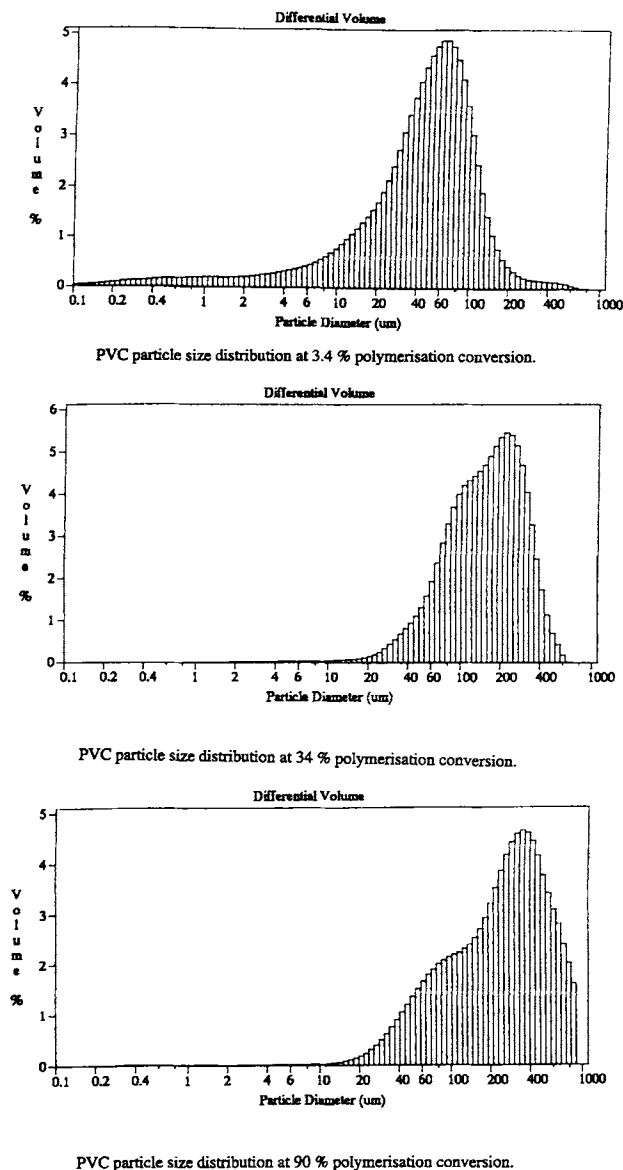PVC particle size distribution at 90 % polymerisation conversion.

Figure 7 Particle size distributions at different polymerization conversions.

was 500 rpm. The procedure consisted of mixing the noncolored VCM and the continuous phase (using the agitator) for a certain time t_i and then adding the dyed VCM. Photographs were then taken at different time intervals and the ratio of the volume of the dyed droplets (V_c) to the total volume of VC present in the reactor $(V_i + V_c)$ was determined. Figure 1 shows the variation of the latter ratio with the stirring time of the mixture t (colored + noncolored) for different premixing time t_i (stirring time of the noncolored droplets prior to the addition of the colored VCM). The figure shows that the rate of coalescence for small values of premixing time t_i
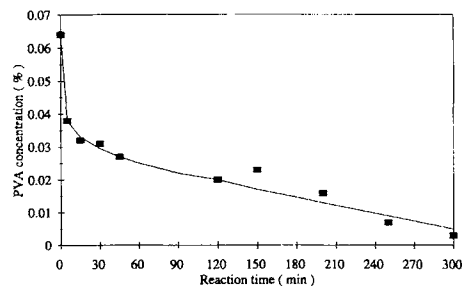

Figure 8 Variation of PVA (72.5% hydrolysis) concentration in the continuous phase with reaction time during vinyl chloride suspension polymerization.

(5 and 15 min) is relatively high; for values of t_i equal to or greater than 30 min, the coalescence rate is lower. This is because the premixing time necessary for the drops to become relatively stable is about 30 min.[17] The shape of the curves in Figure 1 shows that there are two different stages: a first stage of relatively high coalescence rate for mixing times of less than 30 min, and then a second stage where the coalescence rate is lower. Coalescence during the second stage is more pronounced when the premixing time is small. This phenomenon is explicable because, even when the noncolored droplets are stable, the added dyed droplets are not stable initially and need the same mixing time as the noncolored drops to become stable, and thus become more protected against coalescence. A later figure shows what happens when the dyed VC droplets are added to a preformed noncolored suspension.

The second parameter to be studied was the effect of suspending agent concentration (C_{PVA}) on the coalescence rate. For this, the noncolored droplets were premixed (at 500 rpm) for 30 min before forcing the dyed VCM into the reactor. Four experiments were performed using PVA concentrations of 0.002,
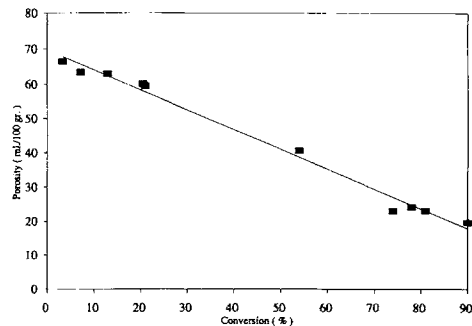

Figure 9 Variation of PVC porosity with conversion in suspension polymerization. $T = 55°C$, volume fraction $= 0.1$, initiator concentration $= 0.175\%$, and C_{PVA} (72.5% hydrolysis) $= 0.06\%$.
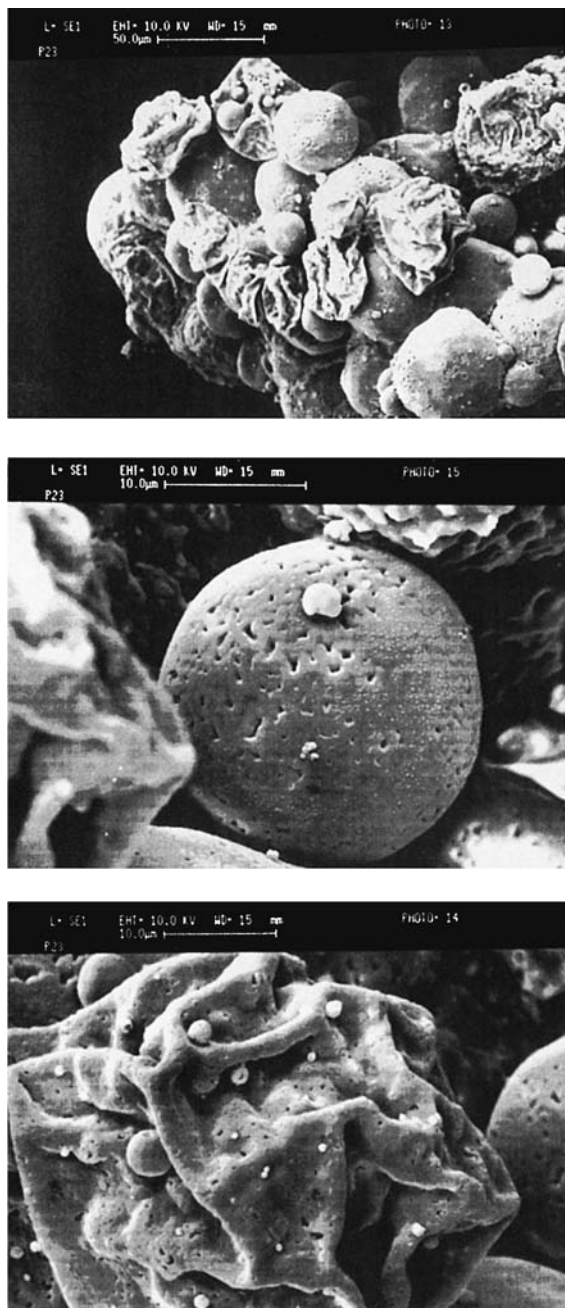
Figure 10   SEM photographs of suspension PVC particles produced using suspension PVC particles produced using suspended initiator predispersed in the continuous phase.

0.01, 0.02, and 0.1%, respectively. Figure 2 shows the variation of $V_c/(V_c + V_i)$ with mixing time t at different PVA (72.5% hydrolysis) concentrations. From Figure 2 we distinguish two different set of curves. For low PVA concentrations (i.e., C_{PVA} = 0.002, 0.01%), most droplets coalesce after 15 min. This is due to the fact that the quantities of PVA available in the continuous phase are not enough to

protect the VCM droplets (the critical concentration was found to be about 0.012%[17,18]), adding to the instability of the dyed droplets at the initial stages. At relatively high PVA concentrations (V_{PVA} = 0.02, 0.10%), the coalescence rate seems to be much lower because there is sufficient PVA to cover the droplets and protect them against coalescence. These results confirm the previous suggestions that the amount of stabilizer plays an important role in controlling the coalescence rate as well as the droplet size and size distribution.

The third parameter to be studied was the effect of turbulence intensity on the coalescence rate. The experimental procedure used in these experiments was similar to the procedure described above (i.e., 30 min for premixing time). The concentration of PVA used was 0.02%. Three experiments were performed using an agitator speed of 250, 350, and 500 rpm, respectively. Figure 3 shows the variation of $V_i/(V_c + V_i)$ with time at different agitator speeds. For an agitator speed of 500 rpm, the coalescence rate is relatively high (all the droplets became colored after 90 min); for lower agitator speeds (N = 250 and 350 rpm), the coalescence rate is quite low. These results show that an increase in the turbulence intensity increases the breakage rate as well as the coalescence rate. It is also interesting to note that for an agitator speed of 500 rpm, the coalescence rate decreased after a stirring time of 30 min (two different slopes on the curve, Fig. 3) while for lower agitator speeds the latter effect is not observed. In conclusion, from these series of experiments it was found that the coalescence rate rises relatively slowly with stirring time (t) and premixing time (t_i), is roughly proportional to the agitator speed, and decreases sharply when increasing the concentration of suspending agent.

Coalescence Rate Study Using H80 as Suspending Agent

In some experiments H80 (degree of hydrolysis 80%) was used as stabilizer. The experimental procedure was the same as described above. The noncolored VC droplets (100 g) were premixed at 350 rpm for 30 min to stabilize them. Then about 30 g dyed droplets was forced into the reactor. Figure 4(A) shows drops at different time intervals from which the total volume of colored and noncolored drops was determined. Figure 5 shows the variation of $V_c/$ $(V_c + V_i)$ with stirring time (t) of the dyed droplets. Also plotted in this figure are the results obtained using H72 as stabilizer. This figure shows that H80 is much more efficient in stabilizing the VCM drop-
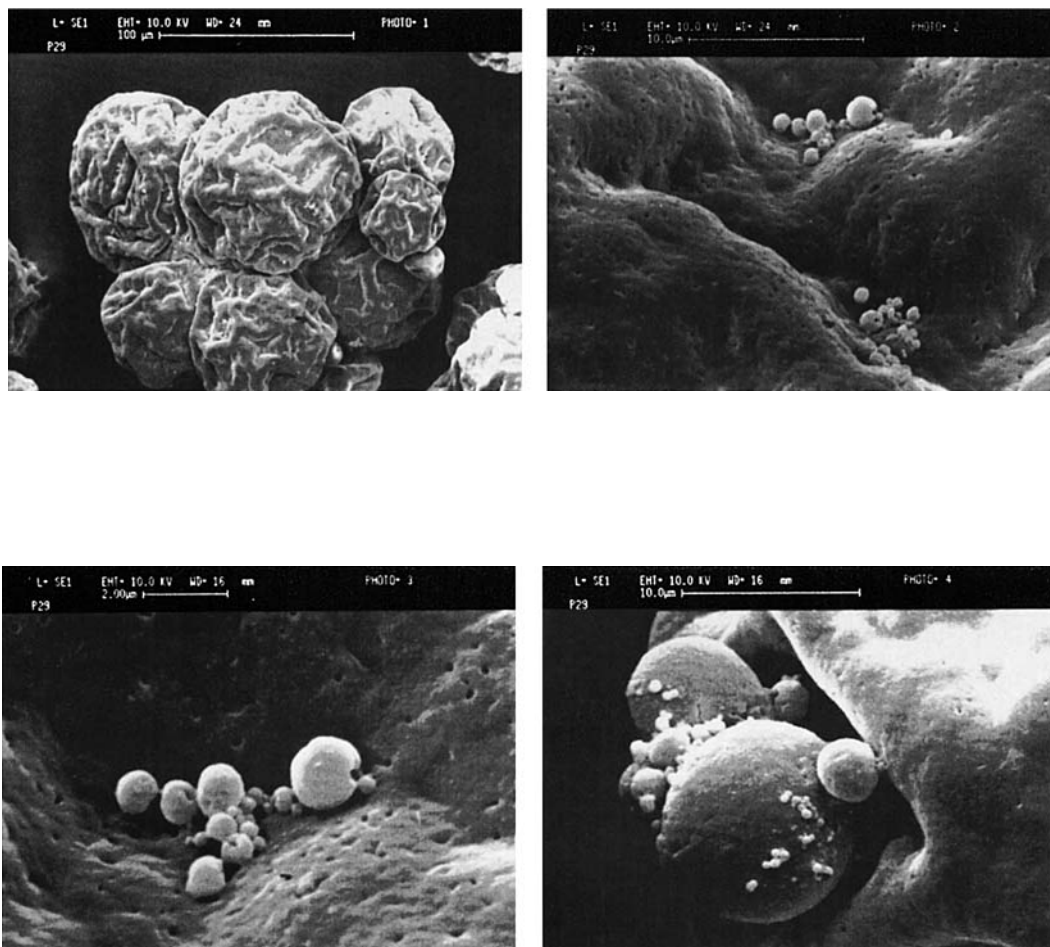
Figure 11 SEM photographs of suspension PVC particles produced using solid initiator predissolved in the vinyl chloride monomer.

lets as the coalescence rate is relatively very low compared with H72 stabilizer. During the initial stages of the mixing operation (i.e., up to about 45 min), the two curves show a similar coalescence rate; but later (i.e., for a mixing time of more than 45 min), the coalescence rate remains low for H80 but increases for H72. Thus, to enhance the segregation between the VCM droplets, it is preferable to use H80 (which has a higher degree of hydrolysis).

Effect of Method of Addition of Initiator on Conversion

The aim of this series of polymerization experiments was to investigate the effect of the method of addition of initiator on the degree of conversion of the VCM. For this purpose, two sets of experiments were performed. The first set of experiments consisted of determining the conversion vs. time using bis(4-*t*-

butylcyclohexyl)peroxydicarbonate initiator predispersed in the continuous aqueous phase and investigating the kinetics of adsorption of PVA (H72) at the droplet/water interface during the suspension polymerization reaction. The aim of the second set of experiments was to compare the conversion vs. time values obtained from the aqueous initiator addition with conversion vs. time values obtained when the initiator was predissolved in VCM prior to reaction. Figure 6 shows the variation of VCM conversion (to PVC) with reaction time. It shows that for the same reaction time, by predissolving the initiator in VCM, the conversion is increased distinctly. This is because the initiator is uniformly distributed between the VCM droplets, enabling them to polymerize uniformly from the beginning of the reaction. This was not the case when the initiator was predispersed in the continuous phase because then some drops did not get enough initiator to poly-

merize uniformly and were at different degrees of conversion. The drops wait for a relatively long time to get some initiator, either from the continuous phase (latex particles, diffusion of free radicals) or by coalescing with other polymerizing VCM droplets at later stages of the polymerization reaction. Table I shows the percentile particle sizes by cumulative percent volume for each polymerization conversion when the initiator was dispersed in the continuous phase. The results presented in the table show that above 20% conversion, the coalescence between the polymerizing droplets becomes very significant. The addition of a secondary stabilizer might help to maintain a relatively constant drop size throughout the polymerization reaction. Particle size distributions for different conversions are presented in Figure 7. These results show a monomodal distribution with the maximum particle diameter moving toward higher values for higher conversions.

PVA Adsorption

Figure 8 shows the variation of PVA concentration in the continuous phase with the polymerization reaction time. From this figure we observe a sharp decrease in PVA concentration in the continuous phase at the early stages of the conversion (during the first 5 min) where about half the initial PVA is adsorbed, and then a slow steady decrease afterward. When the reaction is completed (i.e., $\approx$ 90% conversion), about 95% of the initial PVA is adsorbed from the aqueous phase. The initial sharp decrease in the PVA concentration in the continuous phase is probably due to the formation of the thin "skin" at the droplets' interface at the very early stages of the polymerization ($\approx$ 2% conversion). Allsopp[19] suggested that the relatively high adsorption rate (compared with the case when reaction is not taking place[17,18]) is due to the nature of the interfacially adsorbed polymer, which lowers the covering power of the PVA; thus, more is adsorbed from the aqueous phase. The skin formation is believed to be formed from a graft copolymer (PVA–PVC) transforming the adsorbed stabilizer (PVA) into a rigid layer of about 10-nm thickness.[20]

Particle Porosity

Figure 9 shows the variation of PVC porosity (measured using the cold plasticizer method) with the degree of conversion. It shows a linear decrease in porosity when conversion increases. The results obtained are in good agreement with the findings of other workers.[21] When the conversion increases, the volume of free VCM inside the droplets decreases, thus the primary particles inside the droplets increase in size and become subjected to strong capillary forces that force them to fuse together. This fusion of the primary particles together with the shrinking of the VC swollen PVC particles (which takes place after 70% conversion) are the main causes for the decrease in PVC porosity. Figure 10 shows photographs of PVC particles obtained by using the SEM (scanning electron microscope) technique. These particles were produced by predispersing the initiator (in liquid suspensions) in the continuous phase prior to the addition of VCM and polymerization. Because some droplets get more initiator than others, the final product is a mixture of nonuniform particles with some perfectly spherical and others totally collapsed. When the initiator is uniformly distributed (solid initiator powder predissolved in VCM), the final particles are more uniform in shape as seen in Figure 11. In both cases, the outside surface is relatively smooth and there are some latex particles adhering to the surface of the "normal" particles. Also, a uniform distribution of the macropores can be observed at the surface of the particles.

CONCLUSIONS

This experimental study was devoted to the investigation of the mass transfer (mainly by coalescence) between the VCM droplets for different experimental conditions. It was found that the rate of coalescence rises relatively slowly with mixing time (t) and premixing time (t_i), is roughly proportional to the agitator speed, and decreases sharply when the concentration of suspending agent is increased. Thus, the degree of coalescence is mainly controlled by the mixing time, the agitator speed, and the type and concentration of suspending agent.

The method of addition of initiator has an important effect on the uniformity of the droplets. When the initiator is predissolved in the VCM, the polymerization occurs uniformly in all the droplets and the final particles have the same shape. In contrast, when the initiator is predispersed in the continuous phase, the shape of the PVC particles is not uniform. Some are perfectly spherical while others are totally collapsed. Also, for the same reaction time, the conversion is higher when the initiator is predissolved in the VCM. Furthermore, in the latter case more latex particles are observed.

During polymerization, the concentration of PVA in the aqueous phase decreased substantially and the porosity of the polymer particles was reduced.

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