

# Suspended Emulsion, A New Process for Vinyl Chloride Polymerization: Morphology Control Through Surface Active Additives

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## SYNOPSIS

Suspended emulsion is a new polymerization process in which a water phase containing the initiator is suspended in an organic phase containing the monomer; the polymer formed is insoluble in both the organic and water phases. The final morphology of the polymer is a powder of grains (around 100–300 microns) formed with agglomerates of primary particles (around 1 micron). This article describes the effects of small amounts of either suspending agents (water-soluble polymers) or surfactants. These effects concern mainly the morphology (grain and particle size), but also the polymerization kinetics. A rather homogeneous distribution of grains and particles inside the grain may be obtained by using a cellulosic polymer as the suspending agent and an anionic surfactant such as sodium dodecyl sulfate.

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## INTRODUCTION

Poly(vinyl chloride) (PVC) is an important commodity polymer that is prepared industrially in huge amounts, using various radical polymerization processes. The main process is suspension polymerization using water-soluble polymers such as cellulosic derivatives or poly(vinyl alcohol) as suspending agents, which stabilize first the monomer droplets of the organic phase dispersed through efficient stirring and, later on, the polymer grains; a bulk precipitation polymerization takes place inside the monomer droplets. According to the adopted nomenclature, microdomains (10–20 nm in size) are formed under precipitation and a first aggregation step of the growing polymer chains. These microdomains soon undergo a second aggregation step to give primary particles (100 nm initially). During the polymerization, these primary particles are growing in size and further give agglomerates inside the grains. A skin of the suspending agent grafted with PVC is formed around the grains (size 50–300

microns). The final grains are more or less porous, according to the polymerization conversion (density difference between the polymer 1.42 and the monomer 0.86), the interfacial tension of the suspending agent system (hydrophilicity of the water-soluble polymer, presence of other nonionic or ionic surfactants), and the aggregation modes of the primary particles (modulated by the stirring mode and intensity, the presence of surfactants, the temperature, etc.). The second important process for commodity polymers is the bulk process, which can lead to the same kind of morphology with microdomains, primary particles, and grains of about the same sizes. The grains are not stabilized by any surfactant; however, their external surface is formed with agglomerates of primary particles more compact than those present inside these grains. The compactness of that skin has probably a mechanical origin upon collision of the grains with other grains under the high stirring conditions experienced by the system in the initial (up to 10% conversion) steps of the process. The internal morphology is comparable with that of the suspension process, the final porosity being governed mainly by the final conversion, but also by the initial stirring conditions as well as by the presence of additives that can modify the

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electrostatic stabilization conditions in the organic medium of the vinyl chloride monomer (VCM).<sup>1</sup>

Emulsion polymerization is a third important process used mainly to produce polymers suitable for plastisol applications and foams. Here, VCM is emulsified in water containing a water-soluble initiator such as potassium persulfate (KPS). Emulsion polymerization takes place, starting in the water phase, and leading to submicronic polymer particles that are stabilized by various kinds of low molecular weight surfactants. After the polymerization, an atomization process is used to slightly agglomerate these polymer particles into grains of suitable size (a few microns) easily dispersed into the plastisol.

The same size of grains can be obtained by a rather new French process named microsuspension, involving a real suspension process (organosoluble initiator dissolved in the monomer droplets) using low molecular weight surfactants and carried out in two steps so as to allow a fine tuning of the grain size.

The new process studied here is named "suspended emulsion." In this process, a water phase is suspended into VCM, mainly by high stirring conditions. The initiator is KPS or a water-soluble redox system so that an emulsion polymerization takes place in the water phase from the dissolved monomer and the radicals coming from the initiator. Very low amounts of surfactants or suspending agents are used so that the stabilization of polymer particles initially formed from the emulsion polymerization is rather poor; then, limited flocculation takes place, giving polymer particles of micron size. The size of the grains is governed by the size of the water droplets, with more or less efficient stabilization by the low amounts of suspending agents. However, it is in the same range of a few hundred microns.

This process has many similarities with the main industrial processes. The polymerization takes place basically by an emulsion mechanism with formation of the radicals in the water phase, the radicals being captured by the existing particles inside that water phase. However, it gives a morphology similar to that of the suspension process by a skin of solid

polymers at their boundary. But, as in the bulk process, the polymer grains are initially suspended in an organic phase of VCM, which progressively disappears upon swelling the polymer formed inside the grain and then polymerizing there. The final medium is a powder of PVC grains that is porous, but, here, the porosity is governed mainly by the amount of water that remains inside the grains between the agglomerates of particles.

In a preliminary publication,<sup>2</sup> we described some of the features of this new process such as the influence of the initiator system, the temperature, and the stirring conditions. In this article, we discuss the effect of surface active agents upon the morphology of the grains. These additives are either water-soluble polymers, as those used in suspension polymerization, or surfactants, as those used in emulsion polymerization, or both polymers and surfactants.

## RESULTS AND DISCUSSION

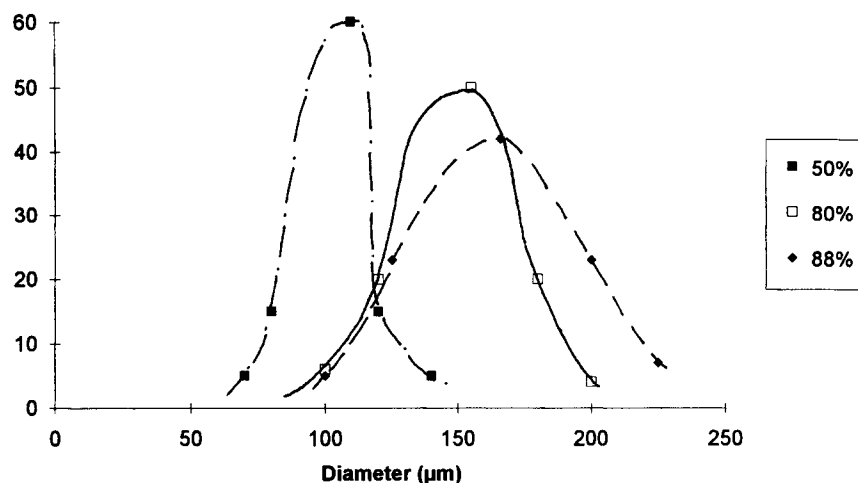
Water-soluble polymers are those usually used in suspension polymerization; it is generally accepted that they are mainly adsorbed on the surface of the organic phase where they constitute a protective film; their role as thickener of the continuous phase is now considered as less important.<sup>3</sup> The main difference in suspended emulsion is that these suspending agents are now soluble in the dispersed phase. So, their effects may be expected to be very different.

A set of experiments has been carried out using PVA with various hydrolysis rates, namely, 50, 80, and 88%. The first one is liposoluble and the two last are water-soluble. A few data about these PVA are reported in Table I. Their effect on the grain-size distribution are shown in Figure 1. Upon increasing the hydrolysis rate, the average size is increased and the distribution becomes broader. However, the presence of the additive strongly reduces the average size, which, in the same conditions (water/monomer ratio = 0.2), should be 260 microns.

**Table I** Characteristics of the Poly(Vinyl alcohol)s Used as Suspending Agents

Trade Name	Source	Hydrolysis Rate (%)	Structure	$M_n$	$M_w/M_n$	Cloud Point
GH 20	Nippon Goshei	88	Bloc	310.000	3.4	> 100°C
KH 17	Nippon Goshei	78.5/81.5	Bloc	60.000	6	45°C
S 202 <sup>a</sup>	Sigma	45/50	Random	30.000	3.9	—

<sup>a</sup> In 58% ethanol solution.



**Figure 1** Grain-size differential distribution from vinyl chloride polymerizations carried out in the presence of poly(vinyl alcohol)s (PVA) (0.5 g/L) and a ratio water/monomer of 0.2. The hydrolysis rate of the PVA are (■) 50%, (□) 80%, and (◆) 88%.

The smaller size is obtained when the additive may be expected to behave simply as a steric stabilizer of the water droplets. Less stabilization is obtained when the additive is the more soluble, which probably means that it is less strongly adsorbed at the interface of the droplets and more partitioned in the water solution. However, the size of the primary particles (0.6 microns) seems not to depend on the nature of the PVA; the part of the PVA that remains in the water phase is expected to be adsorbed onto the primary particles and stabilizes them. Another point to be mentioned is the retardation effect of PVA on the polymerization kinetics. After 1 h polymerization, the conversion, which is 22.5% without additive, is decreased to 12, 8.1, and 6.6%, respectively, in the presence of PVA with a hydrolysis rate of 50, 80, and 88%. Compared with emulsion polymerization, it might be suggested that this retardation effect should be linked with structural defects, such as unsaturated structures coming from side reactions during the synthesis of the PVA.<sup>4</sup>

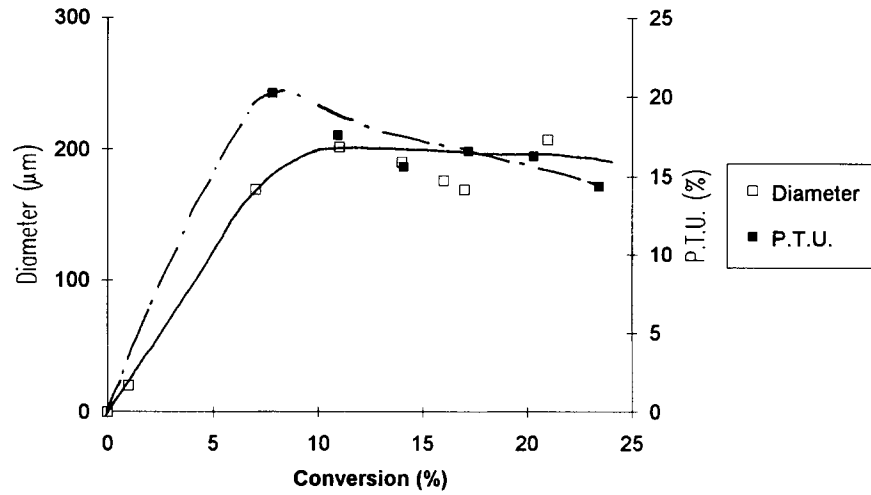
**Table II** Grain and Particle Size for Vinyl Chloride Polymerization in the Presence of Ethyl Hydroxyethyl Cellulose as Suspending Agent and a Ratio of Water/Monomer of 0.4

Ethyl Hydroxyethyl Cellulose (g/L)	Conversion (%)	Grain Diameter (Microns)	Particle Diameter (Microns)
0.5	14	150	1.2
3	16	229	2

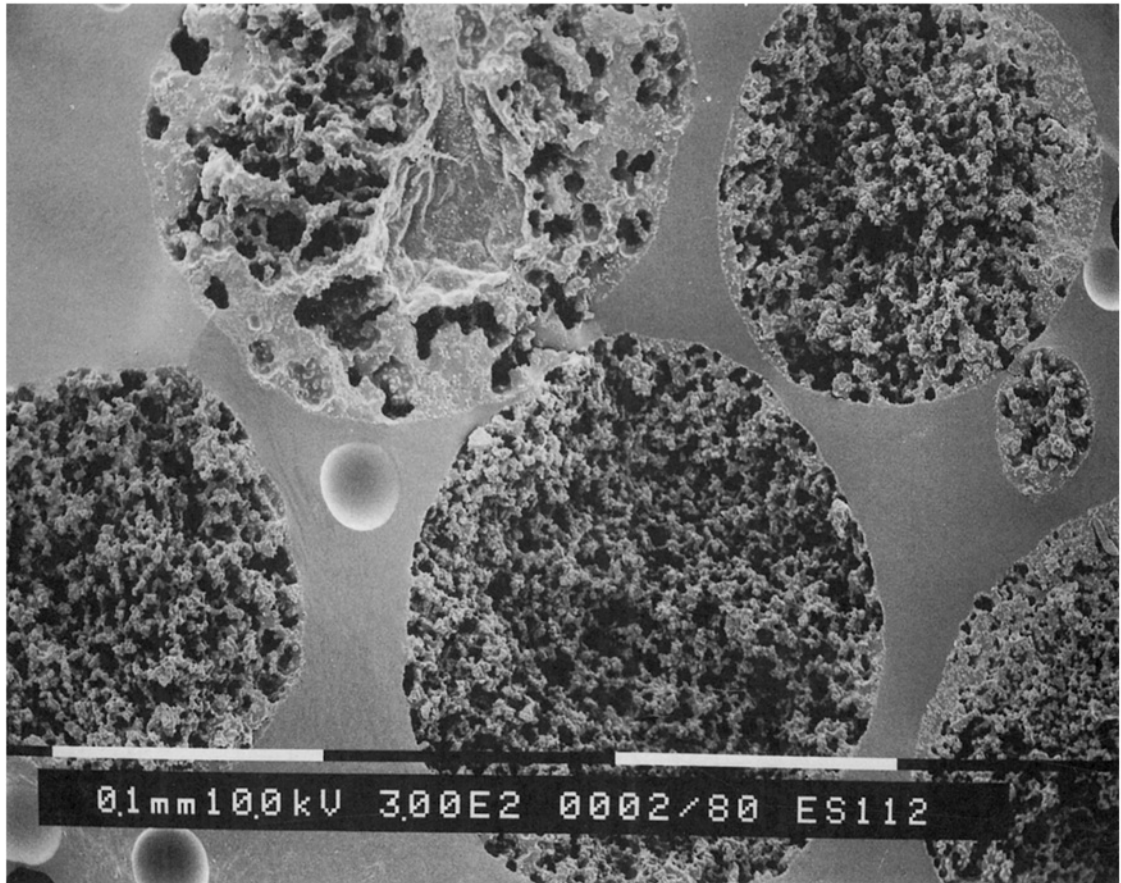
Such a retardation effect is not observed using a cellulosic suspending agent. In that case, too, upon increasing the amount of the water-soluble polymer, both the grain /and the particle size are larger, which may be surprising if one considers that these agents act as surfactants; on the other hand, the major effect might come from increasing the viscosity of the water phase, which make its dispersion more difficult. Typical data are reported in Table II. The reason for the variation of the particle size is more dif-

**Table III** Delayed Addition of a Water Solution

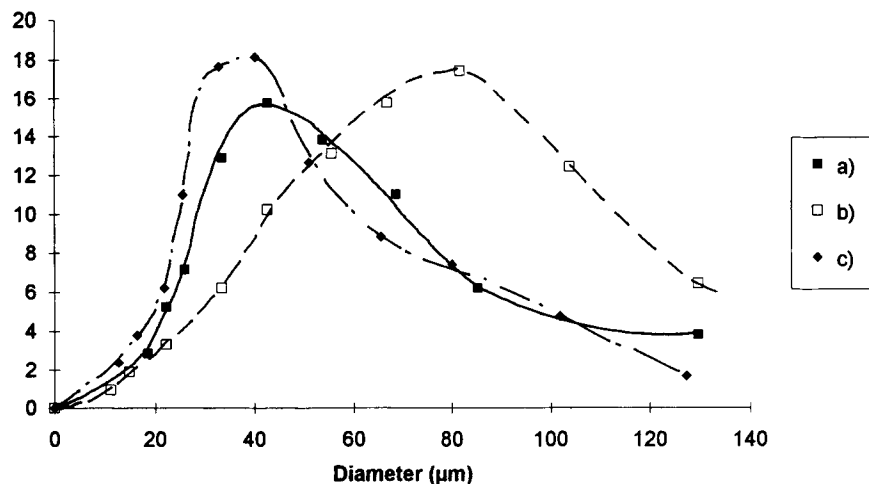
Solution Added		Conversion (%)	Grain Diameter (Microns)
No solution added		2.6	81.9
	water/monomer = 0.33	3.2	88.9
	Final	56.9	87.9
Pure water	Before	1.8	51.9
	After	2.8	65.1
	Final	45.6	81.5
Water + cellulosic	Before	2.0	51.8
	After	3.1	43.7
	Final	48.6	78.7
Water + cellulosic + initiator	Before	2.0	56.1
	After	3.1	50.9
	Final	56.1	86.2
Water + initiator	Before	2.1	55.5
	After	4.8	70.0
	Final	61.1	93.7



**Figure 2** Diameter (□) (microns) and plasticizer uptake (■) (wt %) vs. conversion (%) in a polymerization run using 3 g/L of ethyl hydroxyethyl cellulose and a water/monomer ratio of 0.4.



**Figure 3** Cryogenic cutting of PVC grains obtained by the suspended emulsion process using 3 g/L of ethyl hydroxyethyl cellulose as suspending agent and a water/monomer ratio of 0.4.



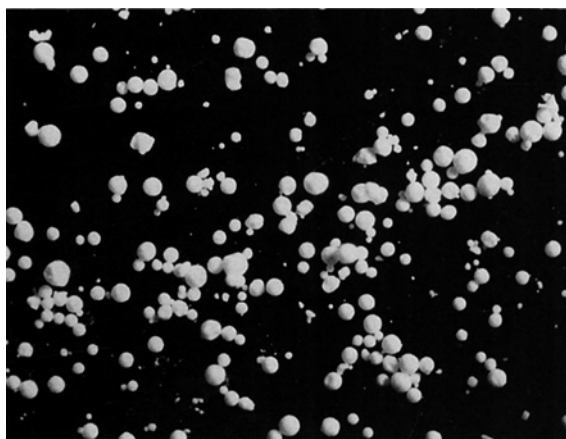
**Figure 4** Grain-size differential distribution (a) without and (b) with delayed addition of water alone and (c) of a solution of the cellulosic suspending agent.

difficult to understand. During the polymerization, the grain size increases between 1 and 6% conversion and then becomes rather stable while the plasticizer uptake slightly decreases, corresponding to a filling process of the grains by the polymer (Fig. 2). A thin skin is observed around the grains, which are more or less homogeneously filled, as shown in Figure 3. Such skin is thinner than the one observed in the PVC suspension polymerization by Davidson and Witenhafer,<sup>5</sup> the thickness of it being near 1 micron. However, such skin is formed rather early in the process after a few percent conversion. The stabilization on the grain size takes place earlier when a suspending agent is used. For instance, in Figure 2, such stabilization is observed after 6% conversion,

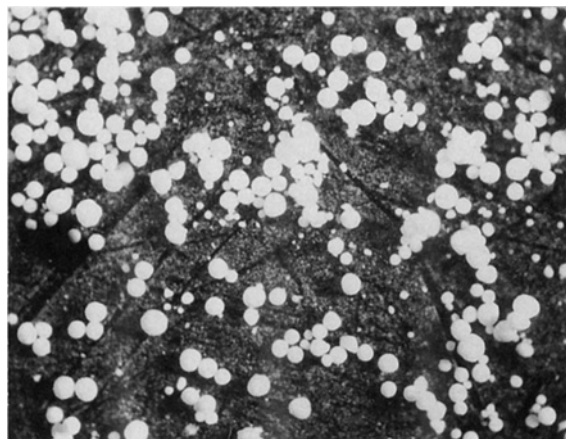
whereas without the suspending agent and using the same recipe, the stabilization takes place around 18% conversion.

Delayed-addition experiments have been carried out to obtain a better understanding of the formation of the morphology. In these experiments, the initial water/monomer ratio was 0.25, and upon addition of a water solution, it comes to 0.33. When water alone is added, the grain-size distribution is shifted toward larger size [Fig. 4(a) and (b)]. There are no new grains formed. Then, water just diffuses through the monomer phase toward the existing grains. If, now, the added solution does contain the cellulosic suspending agent, the change in the grain-size distribution is less obvious [Fig. 4(c)]. How-

a)



b)



**Figure 5** Scanning electron micrograph of PVC from suspended emulsion (a) without delayed addition and (b) with delayed addition of a water solution of the initiator.



**Figure 6** Primary particle of PVC from suspended emulsion polymerization (high magnification: white bar = 1 micron).

ever, the average size of the grains has been decreased from 52 to 44 microns. New grains are formed because the cellulosic molecules added cannot diffuse easily in the monomer phase and they retain at least a part of the water. However, if the added solution does not contain the initiator, some interactions between the new added droplets and the existing grains must take place to allow the transfer of enough initiator for the new droplets to

become grains. Most probably, this transfer process takes place upon collision; it must be indicated here that the addition has been carried out at conversion around 2 or 3%, i.e., before the grain size has been completely stabilized.

When the added solution does contain both the cellulosic compound and the initiator, the distribution is more frankly shifted toward smaller size. New active grains are obviously created more easily.

**Table IV** Effect of Anionic Surfactants on the Grain Size and Conversion in Vinyl Chloride Suspended Emulsion Polymerization (Water/Monomer, 0.076, Time, 5 h)

Name	Concentration (g/L)	Conversion (%)	Diameter (Microns)
Dodecyl benzene sulfonate (DBS)	0.5	20	83
Hexyl sulfosuccinate (Aerosol MA80)	14.6	36	90
Octyl sulfosuccinate (Aerosol OT)	14.6	20	60
Tridecyl sulfosuccinate (Aerosol TR70)	14.6	15	50
No anionic surfactant	—	28	186

**Table V Effect of Nonionic Surfactant (Sorbitan Derivatives) (Concentration 0.5 g/L) on Morphology of PVC Produced in Suspended Emulsion (Water/Monomer, Ratio 0.2; Conversion Around 10%)**

Name of the Sorbitan Derivative	Trade Name	HLB	Grain Diameter (Microns)	Particle Diameter (Microns)
No sorbitan derivate	—	—	180	0.7
Monooleate	Span 80	4.3	246	0.5
Monolaurate	Span 20	8.6	158	0.5
Monostearate polyoxyethylene (20 units)	Tween 60	14.9	118	0.5
Monolaurate polyoxyethylene (20 units)	Tween 20	16.7	138	0.5

Finally, when the added solution contains only initiator (but no suspending agent), the main event seems to be the formation of a new set of fine particles, as shown in Figure 5.

The data corresponding to these delayed addition experiments are reported in Table III. From all these data, it can be concluded that the suspending agent is necessary to obtain grains of large size, but cannot migrate through the monomer phase, as does water. The transfer of the initiator from grain to grain seems possible, probably through a collision mechanism; the new small particles created when more initiator is added after the grain formation process seems not to be captured easily by the existing grains. It must be indicated also that the initial water solution of each run is the same, which means that if the initiator is not present in the added solution the total amount of initiator in the run is smaller; correspondingly, the final conversion is lower and then the final size is normally smaller. Also, the data reported in Table III show that the reproducibility of the first part of the polymerization is not excel-

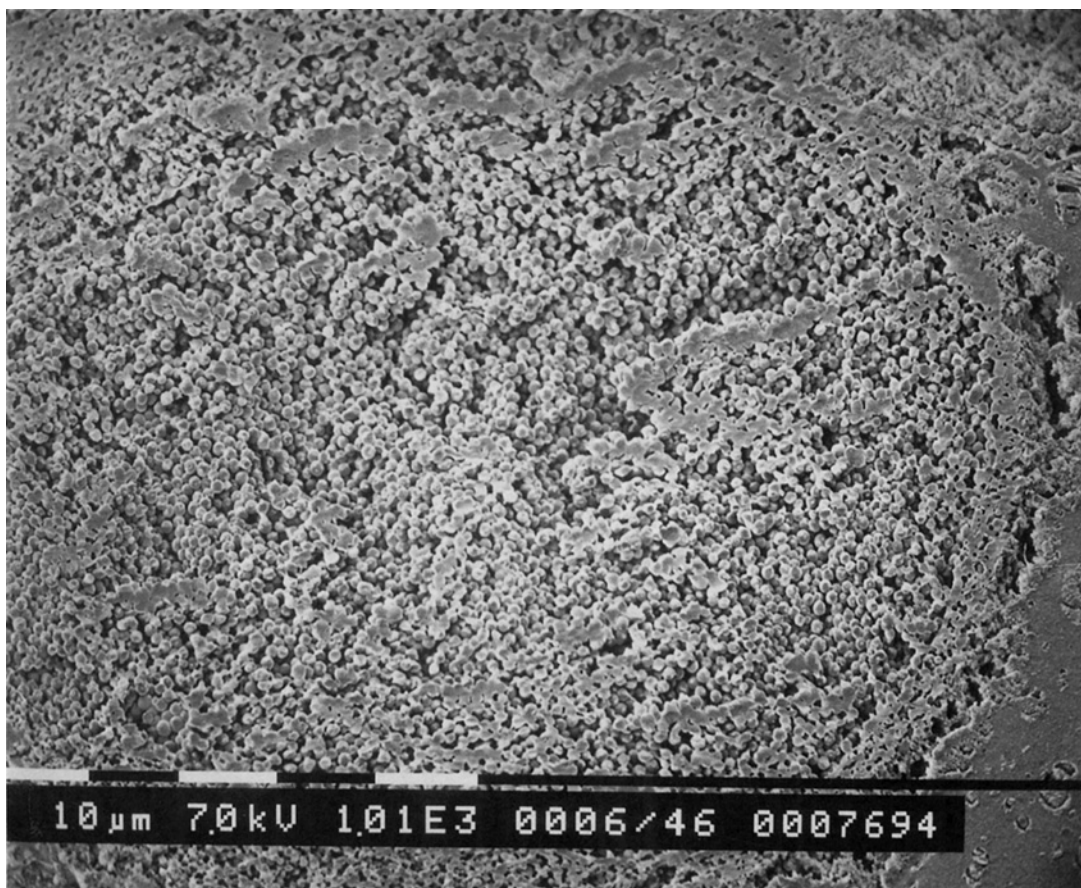
lent, probably because it is very difficult to get it when the initiator system is a redox system and when a temperature program is used.

In the second part of this article, we concentrate on the use of surfactants of low molecular weight such as those currently used in emulsion polymerization. The main difference with a conventional emulsion polymerization is that a part of the surfactant will be present at the monomer/water interface and not only at the polymer particle/water interface. Another point is that in most cases the amount of surfactant is very low, so that the particles formed by the emulsion process are not stable enough and are easily coalesced to give much larger primary particles. Figure 6 well illustrates this coalescence process that takes place early during the polymerization.

Both anionic and nonionic surfactants were used. In the first set of experiments, the suspending agent was omitted. Some typical data are reported Table IV (anionic) and Table V (nonionic surfactants). The effects of these low molecular weight surfactants

**Table VI Suspended Emulsion Polymerization of Vinyl Chloride (Water/Monomer = 0.4) in the Presence of Ethyl Hydroethyl Cellulose (3 g/L) and Surfactants**

Nature	Surfactant Concentration (g/L)	Redox System (ppm)		Conversion (%)	Apparent Density	Plasticizer Uptake (%)	Diameter (Microns)	
		K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	NaS <sub>2</sub> O <sub>5</sub>				Grain	Particle
No surfactant	—	1800	600	65	0.486	21	120	1
DTAB	1.16	1800	600	65	0.55	22	113	3
	3.1 (CMC)	2100	700	64	0.53	33	—	5-10
	15	2400	800	74	0.40	24	—	2-7
NP 30	0.14	1800	600	67	0.49	20	91	2
	0.28	2000	670	65.5	0.53	27	45	2
SDS	0.8	1800	600	72	0.52	18	84	1
	1.6 (CMC)	1500	500	72.5	0.58	24	—	1
	8	450	150	64	0.40	46	—	1



### a) SDS

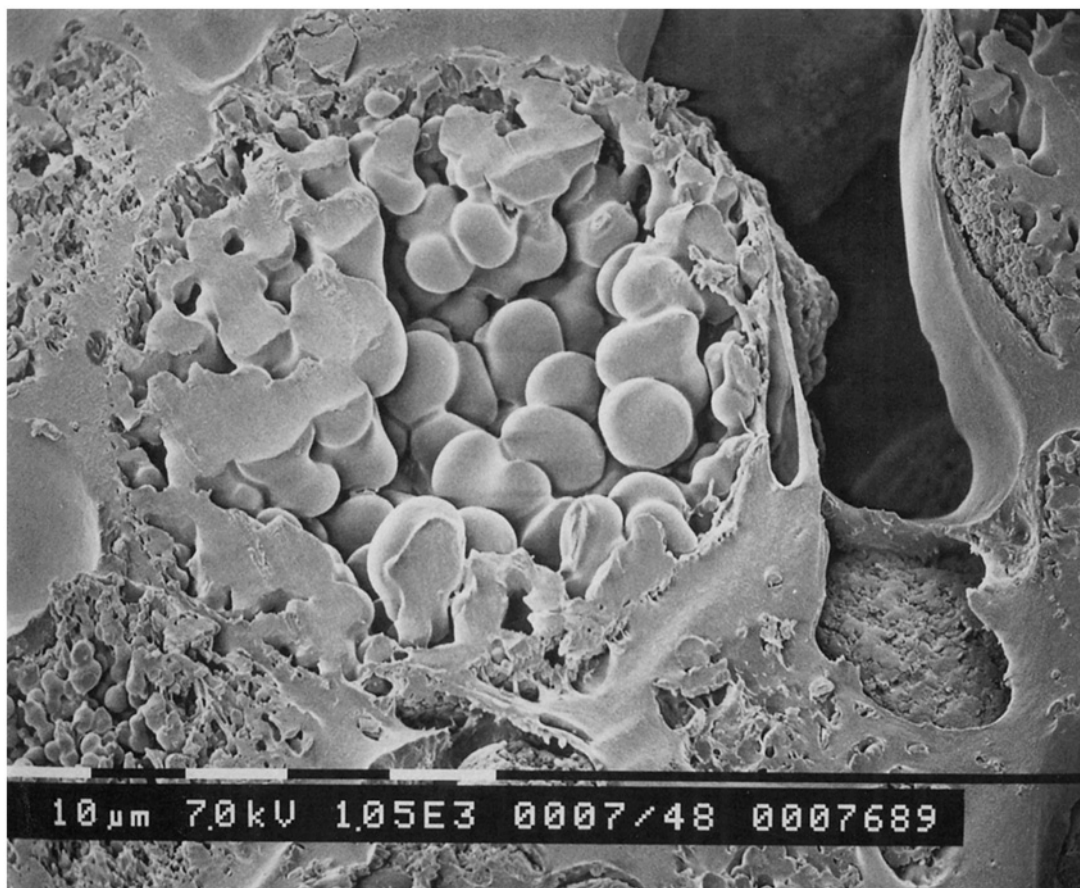
**Figure 7** Scanning electron micrograph of PVC prepared in the presence of surfactants at their critical micellar concentration in the water phase (water/monomer ratio 0.33): (a) sodium dodecyl sulfate (SDS); (b) dodecyl trimethylammonium bromide (DTAB); (c) nonylphenol oxyethylated (NP30).

are very much dependent on their HLB balance, i.e., on their partition between the interface and the two phases. With the anionic surfactant, in low concentration (500 ppm), the average grain size is strongly decreased; however, upon increasing the HLB (shorter alkyl chain), the grain size is increased. A longer alkyl chain is expected to leave less surfactant in the water phase and to stabilize a larger surface area. Then, it can be concluded that these surfactants remain preferentially at the interface between the monomer and the water phase. With the nonionic surfactant, the effect on the grain size is less important, as shown by the lower difference with the experiment where no surfactant was used. Upon increasing the HLB, the grain size goes through a

minimum. The major effect is again that of the length of the alkyl chain, whereas the presence of a longer hydrophilic chain causes a rather small drop in the grain size, without affecting the particle size. It should be noted that the nonionic surfactants have practically no effect on the polymerization kinetics, at variance with the anionic surfactants that strongly increase the polymerization rate if they are much too hydrophilic.

A second set of experiments (Table VI) was carried out in the presence of the cellulosic suspending agent. The three kinds of surfactants, anionic (SDS), cationic (dodecyltrimethylammonium bromide [DTAB]) and nonionic (nonylphenol oxyethylated NP30), have been used at various con-





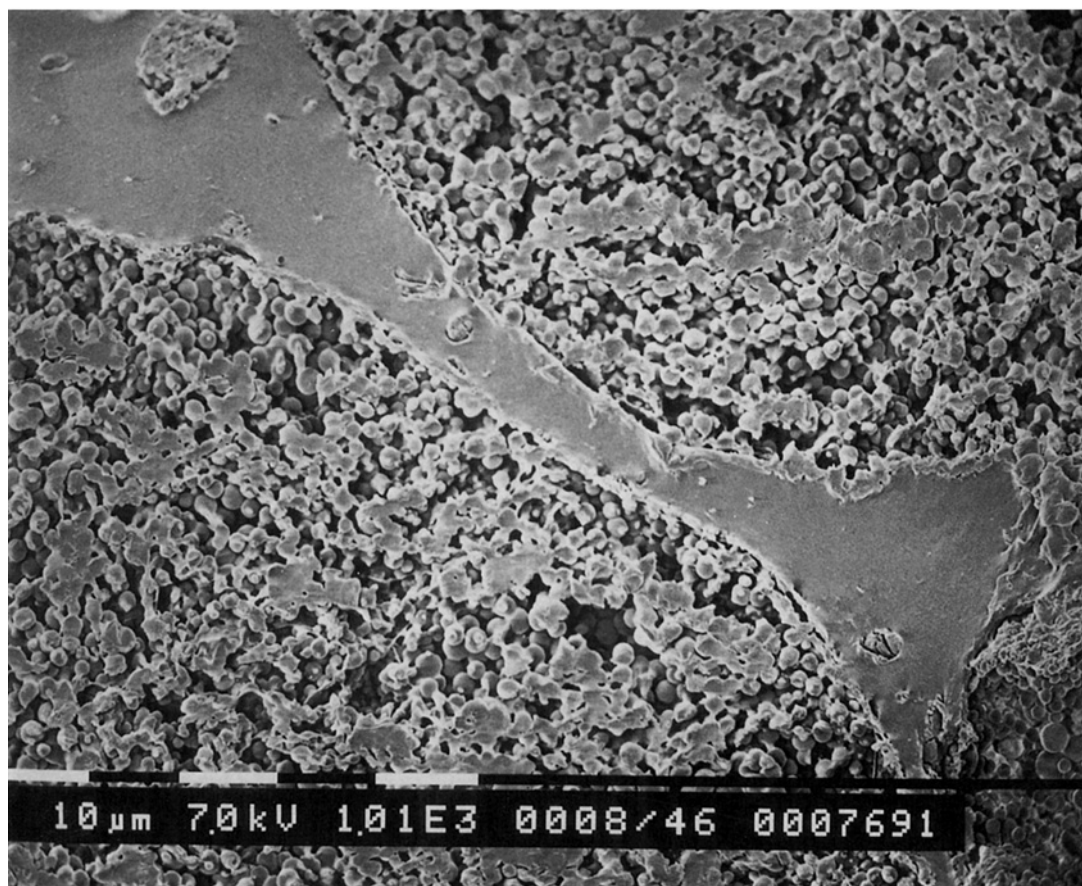
## b) DTAB

**Figure 7** (Continued from the previous page)

centrations, referred to their critical micellar concentrations, which are, at 20°C, 1.6 g/L (SDS), 0.26 g/L (NP30), and 3.1 g/L (DTAB). The amount of initiator has been adjusted so as to have about the same polymerization rate (same conversion after the same polymerization time). No very significant changes in the rate have been observed when either cationic or nonionic surfactants are used; however, in the case of SDS, the rate is very significantly increased, the effect being in line with the amount of surfactant used. This effect may be explained by an increase of the KPS decomposition rate favored by the presence of SDS, as reported by Georgescu et al.<sup>6</sup> But, as we will report elsewhere,<sup>7</sup> this decomposition rate increase is not large enough to explain the big enhancement of the polymerization rate, as shown by the large drop in the initiator concentration to be used when the amount of SDS is higher.

The main effects are in the morphology. The introduction of surfactants cause the grain-size distribution to be very much broader. The average size is decreased in all cases. With either cationic or nonionic surfactants, the particle sizes are rather large and their distribution is broad. A rather large amount of surfactants is necessary to obtain a more convenient homogeneous distribution. However, in the case of SDS, a more homogeneous distribution of particles is obtained, even for low amounts of surfactants.

The effects of the surfactant on the particle morphology are illustrated in Figure 7, where the internal morphology of grains prepared with surfactants at their CMC concentration are shown. Connected to the effect of SDS on the polymerization rate, it can be concluded that the SDS may stabilize many small emulsified particles that can be compartmen-



## c) NP30

**Figure 7** (Continued from the previous page)

talized loci of polymerization. However, at high conversion, these particles tend to coalesce to give the observed primary particles of 1 micron diameter. Nevertheless, upon increasing the amount of SDS, the apparent density is decreased and the plasticizer uptake is increased, which shows that the plasticizer can diffuse more easily in a more homogeneous agglomerated powder. If the SDS is introduced only after the grains have been formed, their size is somewhat smaller and the size of the primary particles is not affected, but the main change is observed with the plasticizer uptake, which is very much decreased while the apparent density is increased. It seems that the grain size stops growing, but the grains become denser internally (Table VII). The same effects are observed if the added solution does contain the initiator, except that new grains of

moderate size (30 microns) are formed in addition to the existing grains.

## CONCLUSIONS

A convenient choice of additives, both suspending agents and anionic surfactants, allows one to control the morphology of the PVC produced in the suspended emulsion. Cellulosic suspending agents must be introduced initially and then, with a convenient water/monomer ratio and stirring conditions, it is possible to fix the grain-size distribution. The internal morphology is much more dependent on the surfactant; it seems possible to obtain high polymerization rates and homogeneous filling of the grain and rather narrow particle-size distribution if

**Table VII Suspended Emulsion Polymerization of Vinyl Chloride (Final Water/Monomer = 0.4) in the Presence of Ethyl Hydroxyethyl Cellulose and Delayed Addition of SDS**

Solution Added	Conversion (%)	Apparent Density	Plasticizer Take-up (%)	Grain Diameter (Microns)	Particle Diameter (Microns)
None	56.9	0.45	35	88	1
Water					
SDS 1.6 g/L	60.0	0.57	8	65	1
Water					
SDS 1.6 g/L					
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 1.8 g/L					
NaS <sub>2</sub> O <sub>5</sub> 0.6 g/L	69.3	0.57	9	68	1

the surfactant is added just after the grain formation process has been completed.

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