The formation of grains of suspension poly(vinyl chloride)

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The development of structure within grains of suspension PVC has been observed by removing samples from an autoclave during a series of polymerizations. Scanning electron micrographs of the samples showed the PVC primaries particles within the grains increased in size as a result of both aggregation and growth. The size also increased with polymerization temperature, but was unaffected by agitation in the autoclave and the type of the protective colloid. A mechanism for the way these factors affect the morphology of the PVC grains has been proposed.

(Keywords: polymerization; aggregation; poly(vinyl chloride); morphology; structure; suspension; primary particles)

INTRODUCTION

Poly(vinyl chloride) is one of the world's most important bulk thermoplastics, approximately 15 million tons being produced annually. About 80% of this is made by the suspension process in which drops of vinyl chloride (VCM), approximately 20 μm diameter, are dispersed in water in a stirred autoclave. During the reaction the droplets, which are stabilized by a protective colloid, agglomerate to give a product consisting of grains approximately 150 μm diameter. Polymerization occurs within the droplets as a result of the thermal decomposition of an oil soluble initiator. Although it is swollen by VCM, the polymer is insoluble in its monomer and immediately precipitates to form microdomains or basic particles approximately 10 nm diameter. These particles are unstable and rapidly aggregate to give domains or primary nuclei of about 0.1 μm diameter. Initially the domains are stable but by 0.1 to 1% conversion they also aggregate and form primary particles. The primary particles continue to grow at the expense of the monomer and, because PVC is denser than its monomer, the final product consists of grains of PVC approximately 150 μm in diameter, packed with a porous network of primary particle aggregates[1-4].

The processing characteristics of suspension PVC are largely determined by the molecular weight of the polymer and the morphology of the grains. As the molecular weight is reduced, the viscosity of the hot melt decreases and the polymer becomes easier to process, although the strength of the finished article is reduced. Porous grains, which readily absorb plasticizer, are used in flexible applications. Grains with a higher packing density and lower porosity are used in rigid applications, to maximise extruder outputs. Porosity is also important in aiding the removal of unreacted monomer at the end of the polymerization[1].

The molecular weight of PVC is determined by the relative rates of chain propagation and chain transfer to the monomer[1]. It can be controlled by the addition of chain transfer agents or chain extenders, although it is more common to vary the polymerization temperature, usually over the range 50°C–75°C. Increasing the temperature decreases the molecular weight.

The morphology of the grains depends on many factors. These include the agitation in the autoclave, the protective colloid (usually a partially hydrolysed poly(vinyl acetate) (PVA) and/or cellulose ether), secondary stabilizers (such as low hydrolysis PVAs or surfactants) and temperature.

Attempts have been made to correlate the interfacial tension of the protective colloid with the properties of the final polymer[5]. A number of workers have studied the effect of surfactants on the polymerization and related their effect to altering the stability of the PVC primaries[6,7]. However, with the (PVC/VCM) surface area involved, 1–3% surfactant would be required to give adequate surface coverage and so affect the primaries' colloid stability, instead of the 0.1% used in practice. An increased fusion between PVC primaries at higher temperatures has already been observed[2], but no complete explanation for the effect of temperature on product properties has yet been published.

Although studies of the effect of agitation on the morphology of suspension PVC have been carried out[1-3,8], there is as yet no explanation as to the mechanism by which it affects particle porosity.

The present study was aimed at determining how these factors affect the porosity of S–PVC. Much of the existing work on grain formation has involved studying the very early stages of the process. While this work is valuable, it was decided to study the latter stages of the polymerization process. This was achieved by carefully removing and studying samples taken from a suspension polymerization reactor during polymerizations designed to give different types of product.

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EXPERIMENTAL

Polymerization

The polymerizations were carried out in a 160 litre capacity autoclave fitted with a water jacket to control its temperature. The autoclave was baffled and its contents agitated by a stirrer in its base. Experience has shown that this configuration gives polymer similar to that obtained on full scale plants. The autoclave was first charged with demineralized water, the protective colloid and the oil-soluble initiator. Unless otherwise stated the protective colloid was a 72.5% hydrolysed poly(vinyl acetate) and the initiator an alkyl peroxydicarbonate. The autoclave was closed, evacuated, purged with nitrogen and evacuated again to reduce the concentration of residual oxygen. Finally it was charged with vinyl chloride monomer and was heated to the required temperature to initiate the polymerization. The pressure in the autoclave remained constant until about 70% conversion, when all of the free monomer had been consumed and the pressure started to fall. Once the pressure dropped to the required level below the running pressure, the reaction was stopped by venting off unreacted monomer. Residual monomer was stripped from the polymer by heating the autoclave contents to 80°C under vacuum. Excess water was removed by centrifugation and the product was dried in a fluid-bed drier.

Sampling

The samples were removed from the autoclave during the polymerization runs using the apparatus shown in *Figure 1*. This consisted of a $\frac{1}{4}$ inch diameter stainless steel pipe leading from the autoclave into a glass-ended sample cell capable of taking pressure. The sample bomb was connected to a number of services to enable it to be charged and emptied. As far as possible, the method of Behrens[9] was used to remove samples from the autoclave, to minimize the disruption of the grains. A sample of slurry ($\sim$100 ml) was run, under pressure, into cold methanol (500 ml) contained in the stainless steel pipe and the sample cell. The cell was cooled with 'Drikold', solid carbon dioxide. The sample was left for 10–15 min to allow complete mixing of the VCM and methanol, after which it was slowly vented to atmospheric pressure. It was removed from the pressure cell and left for 18 h in a fume cupboard before being washed three times with fresh methanol, filtered and allowed to dry in air.

The conversion at which the sample was removed from the autoclave was estimated by assuming that the rate of polymerization was linear and pressure drop occurred at 70% conversion[10]. Kinetic calculations showed this was a good approximation.

Sample analysis

The mean grain size (*mgs*) of the polymers was measured on a Coulter Particle Size Analyser Model TA II, using a 1000 μm orifice tube[11]. The porosity of the polymers was measured using a Carlo Erba Series 800 Mercury Porosimeter.

The molecular weight of PVC is usually expressed in terms of its *K*-value. The *K*-value is calculated from the flow time of a 0.5% solution of PVC in cyclohexanone in a suspended level Ubbelohde viscometer at 25 ± 0.05°C (International Standard ISO-174-1974(E)). The *K*-values were measured using a Schott Automatic Viscometer.

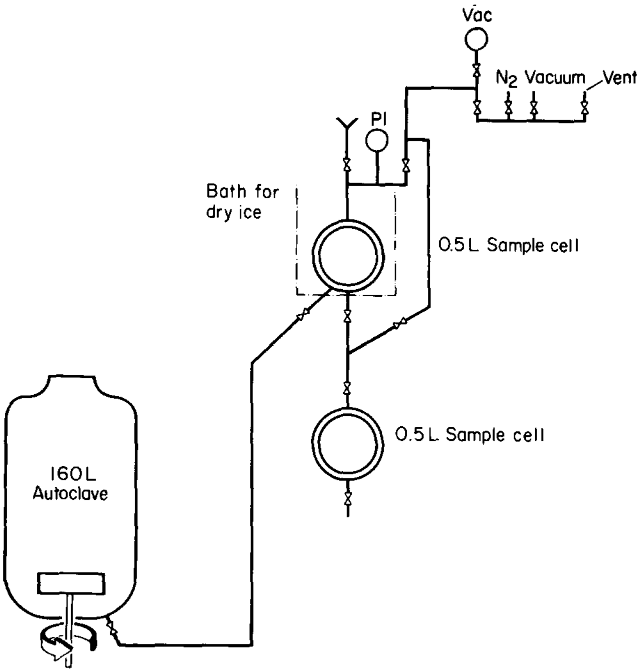

Figure 1 Schematic diagram of the polymerization autoclave and the sampling equipment. The diagram is not drawn to scale

The molecular weight was also determined by means of gel permeation chromatography. Over the normal range of polymerization temperatures temperatures 51°C–71°C the *K* value decreases from 71 to 57. This corresponds to approximate number average molecular weights of 70 000 to 32 000.

The grains were sectioned and prepared for scanning electron microscopy as follows. The grains were soaked overnight in distilled water and, while still wet, supported over the hole in a conventional specimen plate by double sided 'Sellotape'. They were covered with water and rapidly frozen by liquid nitrogen on the stage of a sledge microtome to 77 K. With both the specimen and the glass knife cooled to 77 K, the microtome stage was raised in order to cut a sufficient depth of the sample to reveal diametral planes of the grains. After returning the sample and stage to room temperature the samples were coated with a layer of carbon and of gold. The samples were examined by the normal back scatter mode of scanning electron microscopy, using a Philips 301 EM microscope.

RESULTS

A summary of the polymerization runs carried out with the properties of the final product are given in *Table 1*.

Two runs (K199 and K208) were carried out at 51°C. One of the runs (K208) was carried out at a lower stirrer speed and gave a coarser product with a lower porosity. Three runs were carried out at 57°C. Again the one at the lowest stirrer speed (K127) had the lowest porosity. One of the runs (K214) was carried out using a cellulose ether, instead of PVA protective colloid. One polymerization run (K217) was carried out at 64°C and three at 71°C. The highest temperature polymerizations were carried out with a mixed peroxydicarbonate/lauroyl peroxide initiator system. The control polymer (K138) had a low porosity. The porosity was increased by using a low

Table 1 Polymerization runs

Run No.	Special conditions	Polymerization temperature (°C)	Stirrer speed (rpm)	Properties of final product		
				K value	Mean grain size (μm)	Porosity (ml g^{-1})
K199	–	51	225	71.5	130	0.28
K208	–	51	175	–	152	0.22
K127	–	57	175	67.0	133	0.12
K142	–	57	200	66.5	140	0.17
K214	Cellulose ether colloid	57	225	–	99	0.19
K217	–	64	225	61.2	129	0.14
K138	Peroxydicarbonate/LP initiator	71	220	56.6	135	0.05
K140	Peroxydicarbonate/LP initiator + low hydrolysis PVA	71	200	56.4	152	0.10
K200	Peroxydicarbonate/LP initiator + surfactant	71	175	56.2	136	0.10

hydrolysis (45%) PVA in K140 and a surfactant in K200. The surfactant use in run K200 was the same as that used by Zichy[7] in his 'spinning drop experiments'. It can be seen that the porosity of the PVC decreased with increasing polymerization temperature.

A series of scanning electron micrographs of sections of samples taken from run K127 are shown in *Figure 2*. Micrographs for each sample are given at two magnifications. The low magnification micrograph at 5% conversion shows collapsed individual VCM droplets which have yet to agglomerate. The conversion is low and the amount of polymer present was insufficient to prevent droplet collapse when unreacted VCM was removed during sampling. The VCM droplets contain PVC primary particles surrounded by the droplet skin. The skin is porous and is composed of PVC primaries that have formed or aggregated at the interface. As polymerization continues, the primaries at the interface grow, the skin becomes thicker and the pores disappear.

By 22% conversion the individual VCM droplets have agglomerated to form grains and have retained more of their structure during sampling. The PVC primary particles have increased in size and the grain contains large voids that were filled with VCM. By 58% conversion the primaries are bigger and have formed a continuous network throughout the grain. In the final sample, many of the pores between the primary aggregates have become filled with PVC.

Samples of polymers obtained from other polymerizations were very similar. *Figures 3*, *4* and *5* show sections of grain from a number of other polymerization runs. All of these micrographs are at a similar magnification. The increase in size of the primary aggregates with conversion is clearly visible, along with greater tendency of the primaries to fuse together at higher temperatures.

It was possible to estimate the size of the primary aggregates from each micrograph. The diameter measured was that of each clearly visible or partly coalesced spherical primary. This measurement was carried out manually. One micrograph was examined using the Joyce Loebl Magiscan but the result was essentially similar and was less convenient to obtain[12]. The results, from a representative run at each temperature, are plotted in *Figure 6*. Polymerizations at similar temperatures gave similar results. By estimating the conversion it was possible to calculate the number of primary particles.

The concentration of PVC primary particles (C) at a given conversion (K) was calcaulated as follows:

$$C=\frac{N}{V_{\mathrm{PVC+VCM}}}$$

where N is the number of primary particles and $V_{\mathrm{PVC+VCM}}$ is the total volume of the PVC and VCM phases. The number of PVC primaries (N) is given by:

$$N=\frac{\text{Total weight PVC}}{4/3\pi r^3\rho_{\mathrm{PVC}}}$$

where r is the primary particle radius and ρ_{PVC} is the density of the PVC, so

$$N=\frac{W_{\mathrm{VCM}}\times K}{4/3\pi r^3\rho_{\mathrm{PVC}}}$$

where W_{VCM} is the weight of VCM charged.

As the conversion (K) increases, the density of the polymerizing phase ($\rho_{\mathrm{PVC+VCM}}$) will increase from 0.86 g cm^{-3} to 1.4 g cm^{-3}. At any intermediate conversion, the density will be:

$$\rho_{\mathrm{PVC+VCM}}=(K\times 1.4)+(1-K)0.86$$

$$=0.55\,K+0.86$$

Thus concentration of the primaries,

$$C=\frac{W_{\mathrm{VCM}}\times K}{4/3\pi r^3\rho_{\mathrm{PVC}}}\times\frac{(0.55\,K+0.86)}{W_{\mathrm{VCM}}}$$

$$=(0.55\,K^2+0.86\,K)\times 0.17\times r^{-3}\,\mathrm{cm}^{-3}$$

$$=(0.09\,K^2+0.14\,K)r^{-3}\,\mathrm{cm}^{-3}$$

The decrease in the number of primary particles with conversion is given in *Figure 7*.

The K-values of polymers of different conversions from the same runs is given in *Figure 8*. Results from the other runs lay on the same curves. Samples with a very low conversion gave cloudy solutions in cyclohexanone, presumably because of their relatively high content of protective colloid. The K values of these samples were not

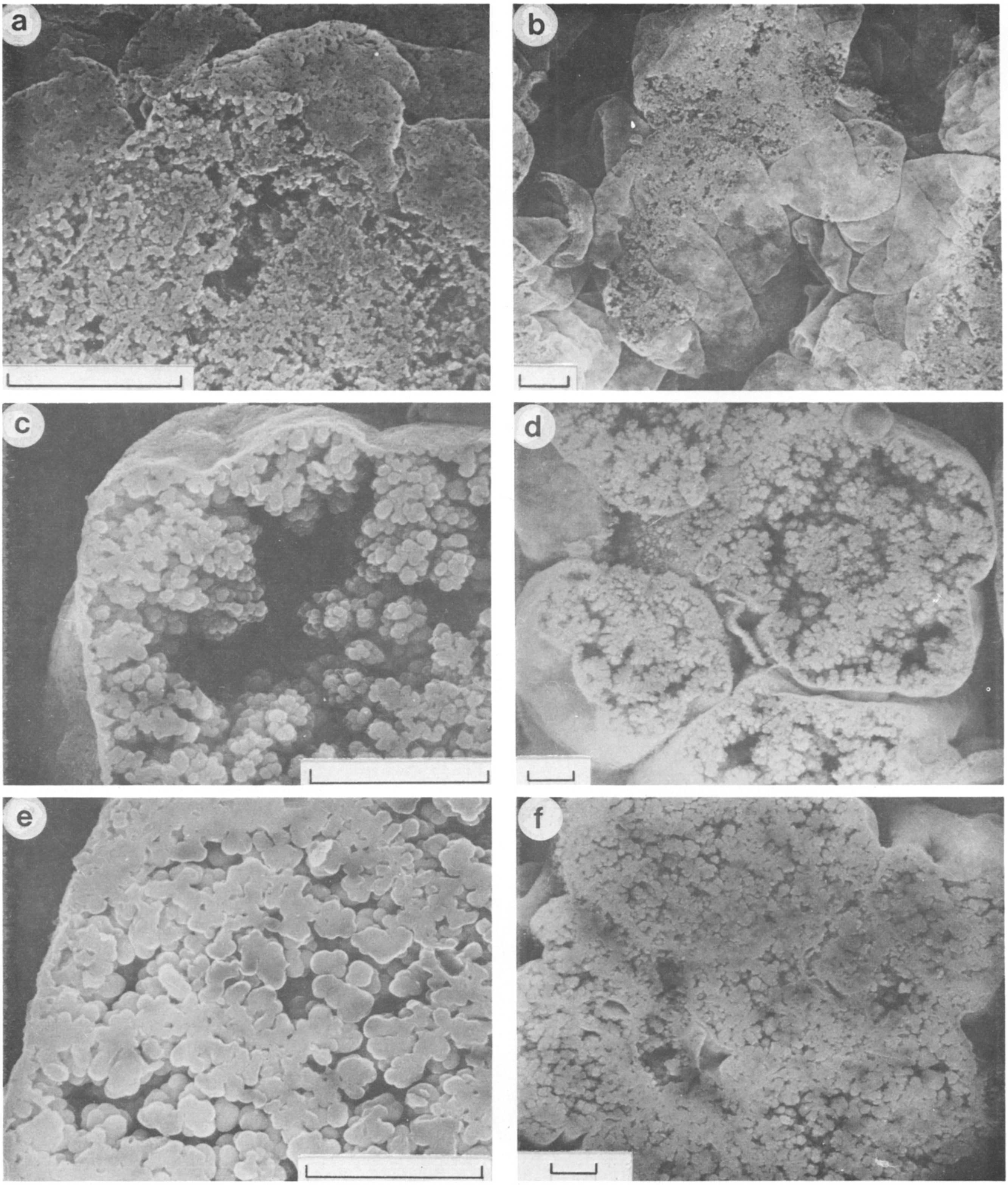

Figure 2 Scanning electron micrographs of sections of S–PVC grains polymerized at 57°C (run K 127): (a) and (b) samples taken at 5% conversion, (c) and (d) samples taken at 22% conversion, (e) and (f) samples taken at 58% conversion. The scale lines represent 10 μm

measured. The g.p.c. molecular weight and tacticity of samples from run K127 are given in *Tables 2* and *3*, respectively.

DISCUSSION

Structure of the surface of the grains

The surface of the VCM droplets, and later the PVC grains, is surrounded by a skin or pericelluar membrane[13,14]. Micrographs of low (<5%) conversion samples show that the skin is composed of PVC primaries very similar in size to those in the bulk of the monomer. Thus they could have either formed directly at the interface or formed in the bulk monomer and aggregated at the interface. Zichy has presented evidence that some polymerization occurs at the interface[7]. Davidson and Witenhafer have presented evidence that the surface primaries can form in the aqueous phase[14]. The gaps

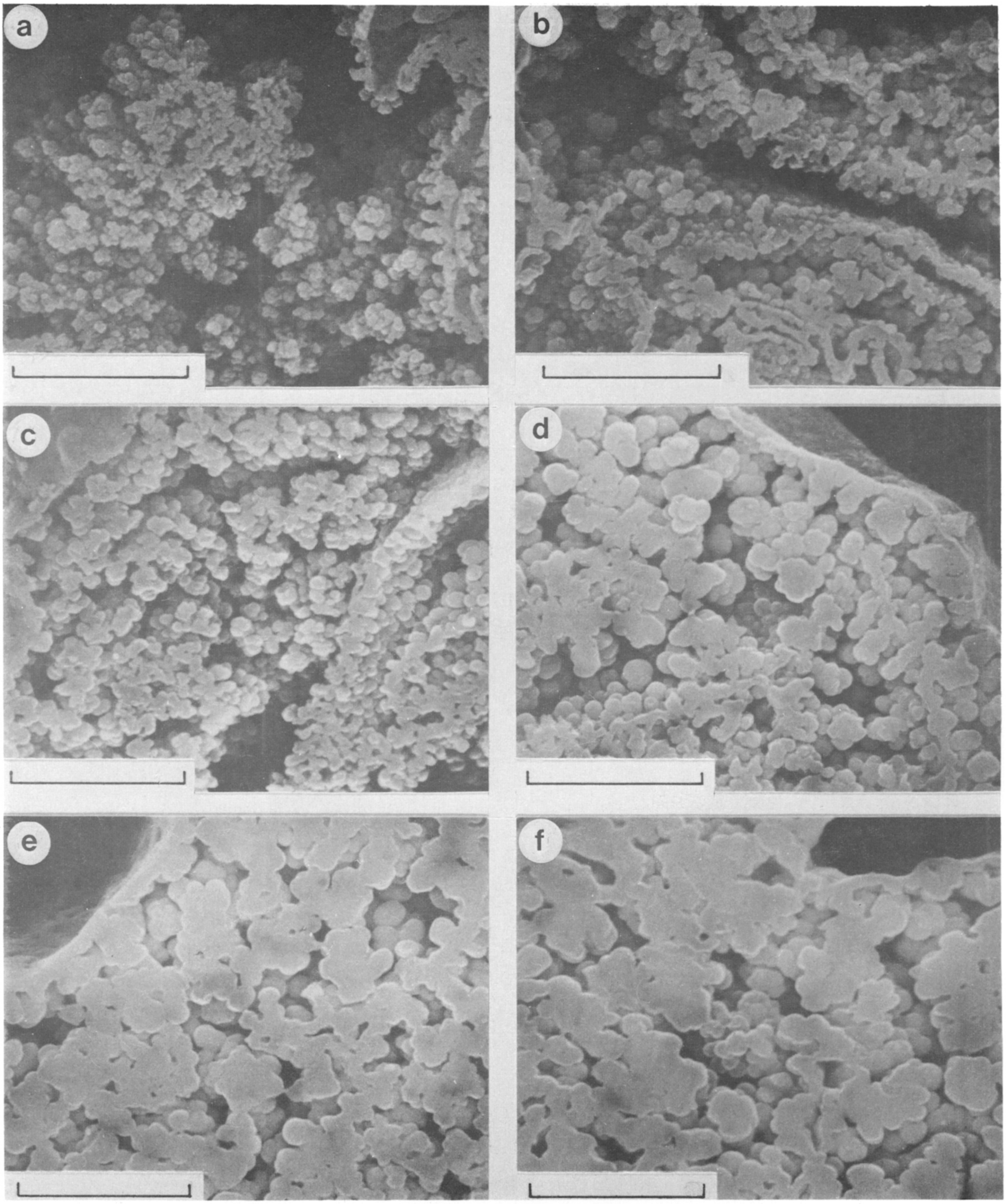

Figure 3 Scanning electron micrographs of sections of S–PVC grains polymerized at 51°C (run K199). The samples were taken at the following conversions: (a) 17%, (b) 29%, (c) 44%, (d) 68%, (e) 77% and (f) 85%. The scale lines represent 10 μm

between the primaries give the skin a porous appearance. As the surface primaries grow, or more particles aggregate at the interface, the skin losses its porosity. It is difficult to quantify, but there is evidence that as the polymerization temperature increases, the skin loses its porosity earlier, between 30 to 50% conversion at 71°C compared with 45 to 75% conversion at 51°C. In the polymerizations at 71°C, in the presence of the low hydrolysis PVA and the surfactant, the skin loses its porosity significantly earlier, by 30% conversion.

The individual VCM droplets agglomerate between 10 to 20% conversion. In subsequent samples the walls of the individual droplets are clearly visible inside the PVC grains. However as polymerization proceeds they fuse

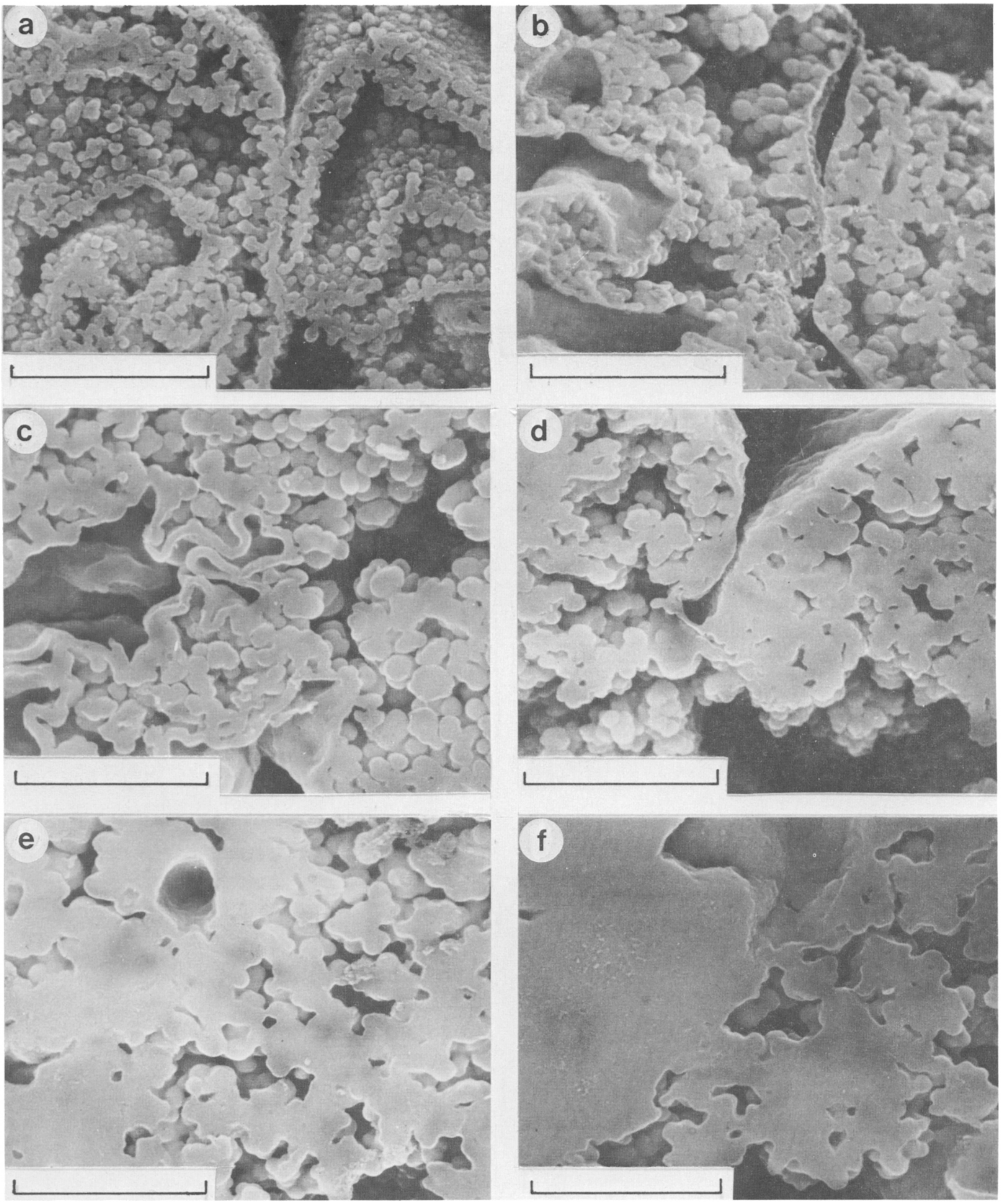

Figure 4 Scanning electron micrographs of sections of S–PVC grains polymerized at 64°C (run K217). The samples were taken at the following conversions: (a) 17%, (b) 29%, (c) 45%, (d) 57%, (e) 79%, (f) 85%. The scale lines represent 10 μm

into the internal structure of the grains and by the end of the polymerization most have lost their identity. The external skin of the grains (pericellular membrane) remains between 0.2 to 0.5 μm thick, even though the primaries inside the grains grow significantly larger. By the end of the polymerization much of this skin has also lost its separate identity.

The presence of a PVA–VCM graft copolymer at the VCM/water interface is well documented[14,15] and its presence has been confirmed in our own laboratories. Although the VCM droplets are coated with a uniform layer of protective colloid, there is no evidence, from the micrographs, for a continuous film surrounding the droplet at low conversion. However the absorbed colloid

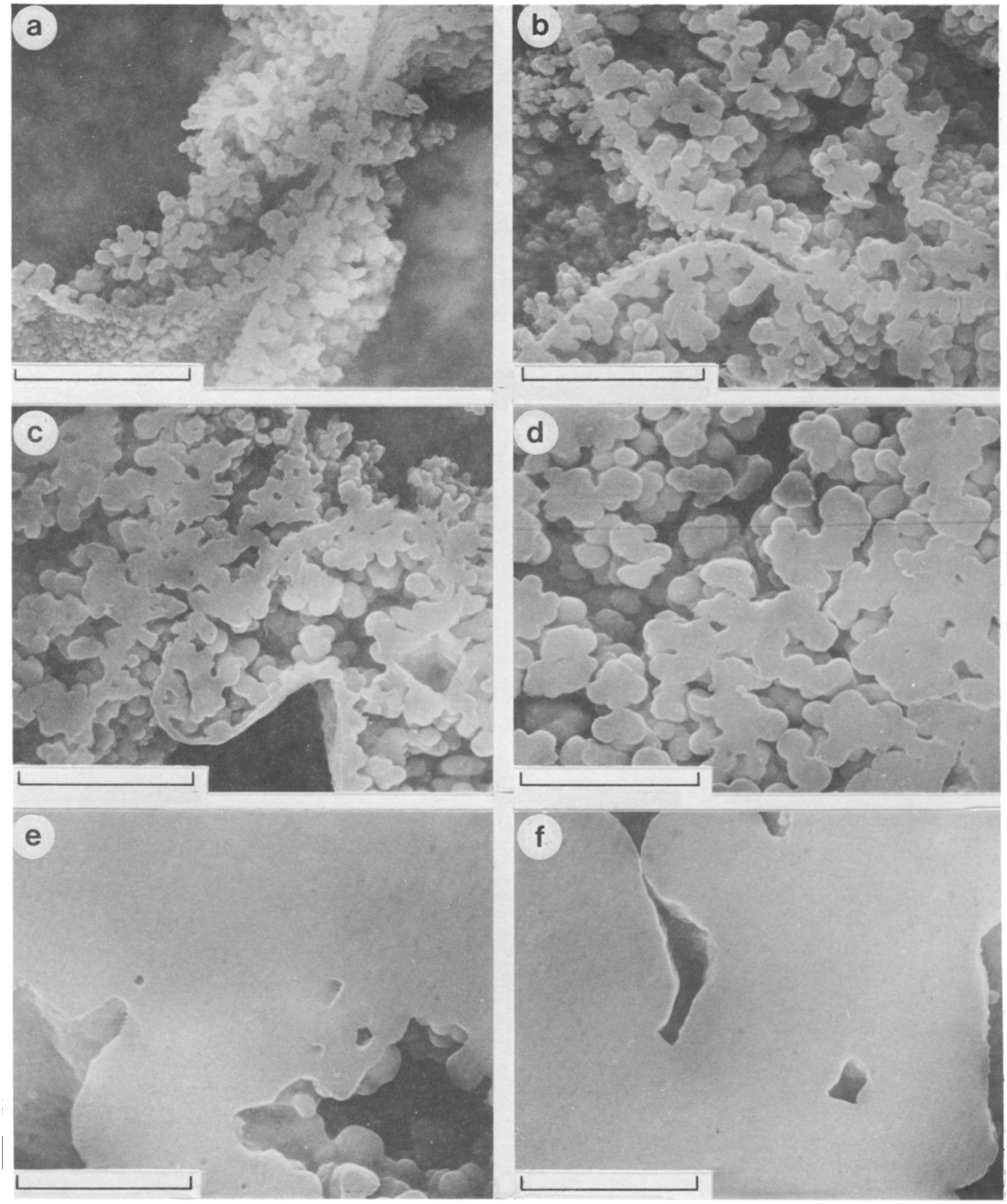

Figure 5 Scanning electron micrographs of sections of S–PVC grains polymerized at 71°C (run K138). The samples were taken at the following conversions: (a) 10%, (b) 20%, (c) 30%, (d) 51%, (e) 73%, (f) 85%. The scale lines represent 10μm

would not have been visible under the electron microscope and a continuous surface layer could have been disrupted during venting. Thus it is not clear whether the graft copolymer is just associated with the primaries at the interface, or is present as a continuous film.

Growth of primaries within the grains

Figure 6 confirms that the size of the primaries increases with conversion. As the polymerization temperature increases, the size of the primary particles at a given conversion also increases. *Figure 7* shows that the primary particles increase in size during polymerization

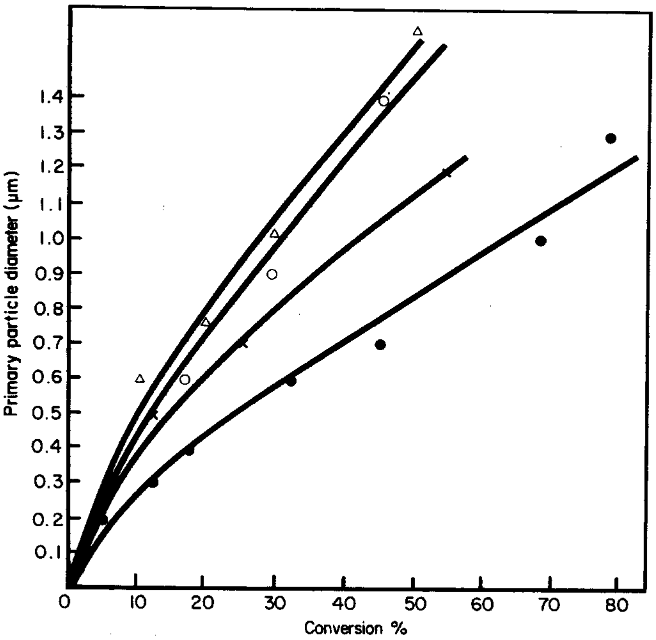

Figure 6 Increase in size of PVC primary particles with conversion. Polymerization at (●) 51°C (K199), (×) 57°C (K142), (○) 64°C (K217) and (△) 71°C (K138), respectively

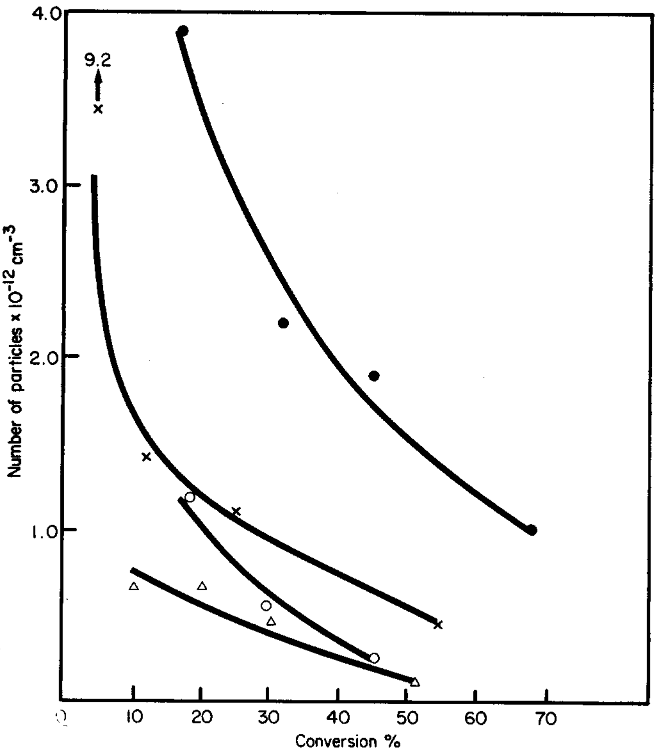

Figure 7 Decrease in number of PVC primary particles with conversion. Polymerization at (●) 51°C (K199), (×) 57°C (K142), (○) 64°C (K217) and (△) 71°C (K138), respectively

as a result of aggregation with other primaries, as well as by the formation of new PVC. At higher polymerization temperatures there are fewer primaries. At all polymerization temperatures the diameter of the primaries tends to the same limiting value at higher conversions, approximately 1.4 µm. The final number of primaries is also similar in all of the runs, approximately 2.0×10^{11} cm^{-3}. In the higher temperature polymerizations the limiting size is reached earlier and the particles then start to fuse together.

One of the most interesting observations from this work is that although polymers made at the same temperature had very different final porosities, the size and number of the primaries was very similar. This was true whether the polymers were made at different stirrer speeds, in the presence of different protective colloids, surfactants or, as some further work has shown, different initiators. Tornell and Uüstalü also found that low hydrolysis PVAs had little effect on primary particle size[6]. There was some evidence that the surfactant used in K200 did give rise to some large unusually spherical primaries, in line with the observations of Zichy[7], although the overall appearance of the grains and the average diameter of the primaries was very similar. Thus these factors do not appear to affect granule porosity by affecting primary particle size.

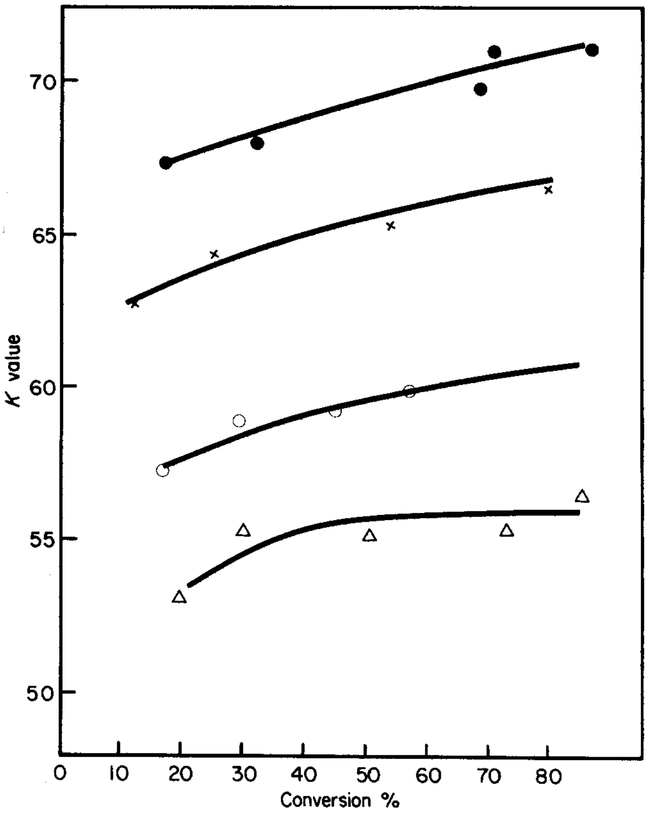

Figure 8 Increase in K value molecular weight of PVC with conversion. Polymerization at (●) 51°C (K199), (×) 57°C (K142), (○) 64°C (K217) and (△) 71°C (K138), respectively

Table 2 The molecular weight of polymer samples from run K127 as measured by g.p.c.

Estimated conversion	M_w	M_n	$D = M_w/M_n$
10%	144 000	63 000	2.3
38%	152 000	68 000	2.2
Final	173 000	75 500	2.3

Table 3 Tacticity of samples from run K127

Estimated conversion	Syndiotactic (rr)	Heterotactic (mr)	Isotactic (mm)
10%	29%	52%	19%
58%	31%	51%	18%
Final	29%	52%	19%

Formation of porosity within the grains

PVC is denser than its monomer ($\rho_{PVC} = 1.4\,g\,cm^{-3}$, $\rho_{VCM} = 0.86\,g\,cm^{-3}$ at 50°C) and thus as polymerization proceeds the VCM droplet will contract. If this continues throughout the polymerization the final grain will be 60% of its original size and will have no porosity.

If the contraction of the droplets is stopped during the polymerization, the continuing contraction of the monomer as it converts to polymer will result in the formation of pores in the final grains. If the droplets underwent no contraction at all, the porosity would be the maximum possible, just over 40%. By analysing micrographs from runs K127, K138 and K140 Sutton[12] has shown that the droplets do stop contracting early in the polymerization. The contraction of the grains could be stopped by the build up of structure in the grain.

In the early stages ($\leqslant 1\%$ conversion) of the polymerization there are a very large number of submicron sized primaries or primary nuclei. The total volume fraction of the polymer is still very low and the primaries move in the monomer as a result of their kinetic energy, by Brownian motion. Occasionally the primaries will collide with each other and some of these contacts will be permanent. The rate of aggregation of the primaries depends on the concentration of the particles, the temperature and the forces of attraction (or repulsion) between the particles[16]. The surface of the primaries is charged[14,17] and various authors have discussed the way their surface charge could affect their colloidal stability[18]. At this stage aggregation will involve contacts between a small number (usually two) primaries.

In the presence of monomer, PVC is swollen with 23% (by weight) of VCM[10]. It thus exists as a gel with a T_g below the polymerization temperature. Bort found the T_g to be −70°C[19], but more recent work by Harrison at Loughborough suggests it could be nearer 0°C.[20] As a result the contacting primaries will deform, and, depending on the mechanical properties of the gel and the surface forces involved[21], could coalesce. In any case, the formation of fresh polymer will rapidly result in the formation of the spherical particles visible in the micrographs.

As the primaries increase in size and the volume fraction of the polymer gel phase increases, aggregation will involve multiparticle contacts. Thus aggregation will result in the formation of a continuous network of primaries throughout the VCM droplet. The formation of such a structure has been postulated by others, notably the Russian School[22,23]. The structure of the flocculated network (i.e. its porosity), its strength and the conversion at which it occurs will depend on the flocculation mechanism, the interactions between the particles, their size and concentration[24]. The strength will also depend on the strength of the PVC gel phase. The continuous network is likely to form between 10–30% conversion, at a similar conversion to that at which the VCM droplets agglomerate.

Depending on its strength, the formation of an aggregated network of primary particles in the grain, could determine the porosity of the final product by resisting the contraction of the grains. Thus the earlier it forms the higher will be the final porosity. However once formed the network will continue to lose porosity as a result of the growth of the primary aggregates, of the infilling of the pores and of the deformation and coalescence of the monomer swollen gel particles[21].

Effect of agitation on porosity

Because of the finite nature of their repulsive energy, electrostatically stabilized dispersions are known to be susceptible to flocculation by shear. Furthermore they become more susceptible to shear-induced flocculation as their size increases[25], mainly because their collision energy is so much greater and is able to overcome their repulsive potential. Thus as the primaries increase in size (as conversion increases) the particles become susceptible to shear-induced flocculation.

Davidson and Witenhafer[14] and others[6,26] have demonstrated that PVC primaries dispersed in VCM flocculate under shear. In the absence of shear the primaries will continue to grow as single particles and provided there is sufficient repulsion between them, will be able to pack closely together without aggregating. This will give rise to a close-packed structure of low porosity, unable to resist droplet contraction. The final product will have a low porosity. In the presence of shear the primaries will aggregate to form a continuous open network at low conversions and the product will have a high porosity.

Strong agitation will also favour the aggregation and agglomeration of the individual VCM droplets present at low conversion. It would be more difficult for droplets in an agglomerate to contract than a single droplet.

Effect of surfactants on porosity

The observation that the secondary stabilizers used in the present study did not affect the size of the primaries suggests that they might have a similar effect on the build up of structure with the grains.

Mason has shown that with liquid droplets suspended in corn syrup[27], little shear was transmitted across the interface, particularly when a surfactant was present. If the same phenomenon occurred in VCM droplets dispersed in water, the PVC primaries would be able to grow without aggregating. The final product would consist of moderately sized spherical PVC grains of low porosity. This type of product is known to be formed under appropriate conditions (low shear with high concentrations of protective colloid)[2].

Many surfactants (including those used in the present work) are adsorbed at the VCM/water interface, along with the primary colloid. They affect the size of the final PVC grains, and the concentration of the primary protective colloid must be adjusted to compensate. Optical microscopy of VCM droplets, dispersed in water in a pressurized observation cell, carried out in this laboratory has shown that the initial VCM droplets are less resistant to coalescence when the protective colloid system contains a low hydrolysis PVA. If the droplets undergo more coalescence or deformation, the primaries they contain will be subjected to greater shear. They will aggregate and form a network earlier and the final product will have a higher porosity. The VCM/water interfacial area is relatively low and only a small amount of surfactant would be needed to achieve this effect.

Some surfactants also increase porosity when injected later in the polymerization[28], by modifying the infilling of the network of primary aggregates. This is due to their altering the interfacial tension between the PVC gel phase and the water or the monomer, which might be expected to alter the filling of pores by unreacted monomer or to modify the contact deformation of the PVC primaries[21].

Effect of polymerization temperature on porosity

The most obvious differences in the micrographs of samples polymerized at low and high temperatures is that the latter have fewer larger primaries and that the primaries appear to coalesce more readily.

The larger primaries could be formed as a result of either the formation of fewer particles at the start of the polymerization or their more rapid earlier aggregation.

There is little experimental evidence as to the effect of temperature on the formation of microdomains at the start of the reaction. It is not thought that the use of a different initiator, or an increase in the rate of formation of initiator radicals at higher temperature, would affect the number and size of the microdomains. Work in these laboratories has shown that increasing the amount of initiator by a factor of about 2, at a constant temperature, and hence altering the flux of initiator radicals, has no effect on the morphology of the final polymer and hence presumably also on the processes occurring in the grains. The more rapid is the rate of polymerization, the more rapidly the microdomains, domains and primary particles form and aggregate. Thus the PVC grain is formed more rapidly, but the way it is formed remains unchanged. Conversion is the important parameter, not time. Thus, provided the increase in initiator concentration is not too large, its only effect is to reduce reaction time.

Increasing the reaction temperature could reduce the colloidal stability of the domains and primary particles thus reducing their number and increasing their size. Experimental studies by Bort[29] and by Boissel and Fisher[30] suggest that the size increases with increasing polymerization temperature, as was found in the present work. Studies on aqueous latex dispersions[24] have shown that the strength of the flocculated network of latices decreases with increasing particle size, as the number of contacts decreases. Thus increasing the size of the PVC primaries might also reduce the strength of the network and enable greater contraction to take place.

Molecular structure of PVC

The results in *Figure 8* show that as conversion increases the K value molecular weight also increases. G.p.c. analysis of samples from run K127 gave similar results (*Table 2*) and also showed that the molecular weight polydispersity ($D = M_w/M_n$) remained constant at about 2.2. Similar results have been obtained by others[31]. It is believed to be caused by the reduced rate of chain termination as an increasing proportion of the polymerization occurs in the higher viscosity polymer gel phase[32].

N.m.r. measurements made on samples removed from run K127 showed that from 5% conversion the tacticity (*Table 3*) of the polymer did not change. X-ray diffraction measurements showed that the crystallinity of all of the samples was 8%, regardless of conversion.

CONCLUSION

A qualitative explanation of the way that agitation, the presence of surfactants and temperature control the morphology of S–PVC has been developed as a result of removing and examining samples from the autoclave during a number of polymerization runs. It involves the formation of a continuous network of flocculated primary particles within the grain between 10 to 30% conversion. The conversion at which this network is formed, its structure and strength, as well as its subsequent infilling, controls the product's final porosity. A model for the mechanism by which agitation, the presence of surfactants and temperature control the formation of the primary network has been suggested and although the process has already been started by Maitland[32], there is still further scope for work to enable these processes to be quantified.

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REFERENCES

1 Burgess, R. H. in 'Manufacturing and Processing of PVC', (Ed. R. H. Burgess), Applied Science Publishers Ltd., London (1982)
2 Allsopp, M. W. in 'Manufacturing and Processing of PVC', (Ed. R. H. Burgess), Applied Science Publishers Ltd., London (1982)
3 Bieringer, H., Flateau, K. and Reise, D. *Makromol. Chem.* 1984, **123/124**, 307
4 Clark, M. in 'Particulate Nature of PVC', (Ed. G. Butters), Applied Science Publishers Ltd., London (1982)
5 Nilsson, H. *et al. J. Vinyl Tech.* 1985, **7**, 123
6 Tornell, B. E. and Uüstalü, J. M. *J. Vinyl Tech.* 1982, **4**, 53
7 Zichy, E. L. *J. Macromol. Sci.–Chem.* 1977, **A11**(7), 1205
8 Johnson, G. R. *J. Vinyl Tech.* 1980, **2**, 138
9 Notzold, G. and Behrens, H. *Plaste Kautsch.* 1978, **10**, 563
10 Berens, A. R. *Makromol. Chem.* 1975, **47**, 97
11 Taubinger, R. P., to be published
12 Sutton, D., personal communication
13 Barclay, L. M. *Makromol. Chem.* 1976, **73**, 1
14 Davidson, J. A. and Witenhafer, D. E. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 51
15 Weber, J., Thummler, W. and Kaltwasser, H. *Plaste Kautsch.* 1983, **30**, 606
16 Heimenz, P. C. 'Principles of Colloid and Surface Chemistry', Marcel Dekker Inc. (1977)
17 Cooper, W. D., Spiers, R. M., Wilson, J. C. and Zichy, E. L. *Polymer* 1979, **20**, 265
18 Willmouth, F. M., Rance, D. G. and Henman, K. M. *Polymer* 1984, **25**, 1185
19 Ibragimov, I. Ya. and Bort, D. N. *Vysokomol. Soedin. Ser. B* 1974, **16**, 376
20 Harrison, E., Loughborough University, to be published
21 Kendall, K. and Padget, J. C. *Int. J. Adhesion Adhesives* 1982, **2**(3), 149
22 Bort, D. N., Kuchanov, S. I. and Zegel'man, V. I. *Polym. Sci. USSR* 1975, **17**, 3151
23 Neimark, A. V. and Kheifets, L. I. *Polym. Sci. USSR* 1981, **23**, 2121
24 Stewart, R. F. and Sutton, D. *Chem. Ind.* 1984, May, 373
25 Buscall, R. and Ottewill, R. H. in 'Polymer Colloids', (Ed. R. Buscall *et al.*), Elsevier Applied Science Publishers (1985)
26 Palma, G. *et al. J. Polym. Sci.* 1977, **15**, 1537
27 Rumscheidt, F. D. and Mason, S. G. *J. Colloid Interface Sci.* 1961, **16**, 210
28 Smallwood, P. V., US Patent 4446287
29 Bort, B. N. *et al. Polym. Sci. USSR* 1967, **9**, 334
30 Boissel, J. and Fischer, N. *J. Macromol. Sci.–Chem.* 1977, **A11**(7), 1249
31 Zajchowski, S. *et al. Polimery* 1980, **25**(3), 94; translated in *Int. Polym. Sci. Technol.* 1980, **7** T, 35
32 Kelsall, D. G. and Maitland, G. C. in 'Polymer Reaction Engineering, Influence of Reaction Engineering on Polymer Properties', (Ed. K. H. Reichert and W. Geisseler), Hanser Publishers, Munich, (1983)