

THE DEVELOPMENT AND IMPORTANCE OF SUSPENSION PVC MORPHOLOGY

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Abstract - A review of the current state of knowledge of suspension PVC morphology is presented and related to changes taking place during polymerisation and in subsequent processing. Morphology is considered in terms of the structures observed in three different size ranges and a mechanism for their formation is suggested.

INTRODUCTION

Each of the large tonnage polymers produced today have particular parameters which must be carefully controlled in order to ensure that the optimum properties of the material are achieved during processing and fabrication processes. Whereas other polymers may be concerned with molecular weight distribution, the rate or level of crystallisation, crystallite size, relative density, melt flow index, etc, the success or otherwise of a PVC polymer depends largely on its grain morphology. With the advent of a number of new techniques it is possible to characterise the morphology of PVC in a much more comprehensive way than was previously possible and this has led to a much greater technical awareness of the importance of morphology, particularly porosity and uniformity with respect to processing behaviour.

In this paper a review of the present state of knowledge of PVC morphology is presented and related to the changes taking place during polymerisation and in subsequent processing.

NOMENCLATURE

In the technical literature the terminology used to describe the morphology of PVC is varied and very confusing. Since it is important to have a clear and unambiguous system of nomenclature this aspect of the subject will be covered in some detail here.

Following the second international symposium on PVC at Lyon-Villeurbanne in 1976 a discussion of the terminology used to describe PVC morphology was summarised and published by Geil (1) in an attempt to obtain consistency. Geil's terminology forms the basis of the system used here, Table 1.

A series of micrographs is included with each species identified in turn, Figs. 1-3.

All these structures can be brought together in the following model of a PVC grain, Fig. 4.

The problem with models of this type is that they are idealised and not drawn to scale. The problem of portraying a realistic model is seen if we just consider the primary, domain and micro-domain morphology drawn to scale, Fig. 5.

Only then can it be appreciated how much growth of the domain or primary nucleus must take place with conversion in order to reach the 0.7 μm primary particles seen in high conversion samples of PVC. Also it suggests that although the domain may be important in terms of the molecular ordering/crystallinity of PVC at low conversion and hence exert a considerable influence on say, rheological properties, it is not a fundamentally important feature of morphological texture of high conversion polymer. For the remainder of this paper it will be considered simply as a primary particle nucleus and the latter term will be used as well as domain to describe this particular species.

TABLE 1. List of PVC nomenclature

Term	Approximate Size		Origin or Description	Previous Terminology (with References)
	Range μm	Average μm		
Grain	50-250	130	Visible constituent of free flowing powders, made up of more than 1 monomer droplet.	Granule (2) Cellular grain (3)
Sub-grain	10-150	40	Polymerised monomer droplet.	Sub granule (2) Unicell (3)
Agglomerate	1-10	5	Formed during early stage of polymerisation by coalescence of primary particles (1-2 μm). Grows with conversion to size shown.	Aggregate (2) Cluster (3) Macro globule (4)
Primary particle	0.6-0.8	0.7	Grows from domain. Formed at low conversion (less than 2%) by coalescence of micro-domain: grows with conversion to size shown.	Microgranule primary particle (2) granule (3) micro-globule (4)
Domain	0.1-0.2	0.2 (200nm) (2000 Å)	Primary particle nucleus. Contains about 10^5 micro-domains. Only observed at low conversion (less than 2%) or after mechanical working. Term only used to describe 0.1 μm species; becomes primary particle as soon as growth starts.	Primary nucleus (2) Granule (3)
Micro-domain	0.01-0.02	0.02	Smallest species so far identified. Aggregate of polymer chains - probably about 50 in number.	Basic particle (2) Particle (3)

Notes on Table 1

- 1 The domain is not a feature of PVC morphology in high conversion polymer samples since a growth of this species with conversion obliterates all memory of it. It may only be "regenerated" and observed after subsequent processing.
- 2 As soon as formation of the domain is complete and growth is registered it is preferable to call it a primary particle. Therefore, the term domain is often ignored in favour of primary particle even at the point of morphogenesis of the 0.2 μm primaries at low conversion.
- 3 The reason for a separate identity for the domain is that it may be shown in future to contain an atypical morphological or molecular feature, eg higher level of crystallinity.

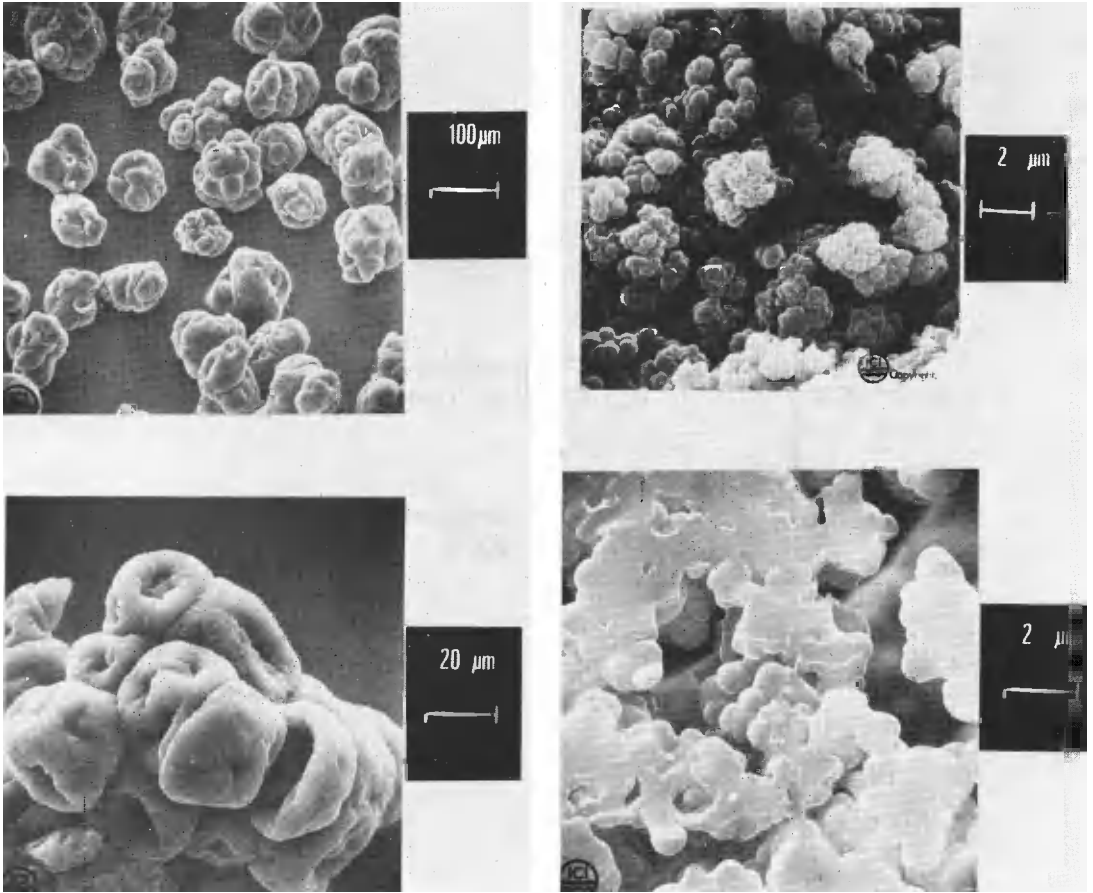
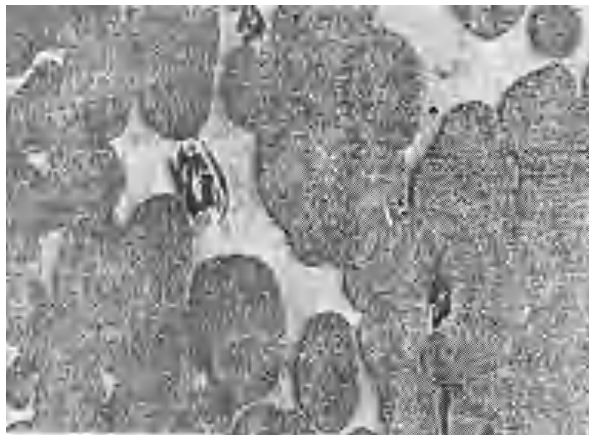


Fig. 1 PVC grains and sub grains.

Fig. 2 PVC primary particles and agglomerates.



TÉM. 0.5μ

Fig. 3 PVC micro domains and primary particles.

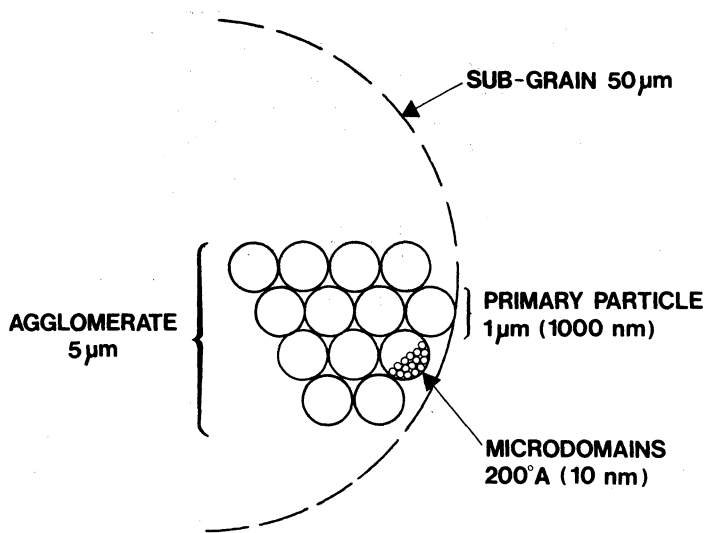


Fig. 4 Model of PVC grain morphology.

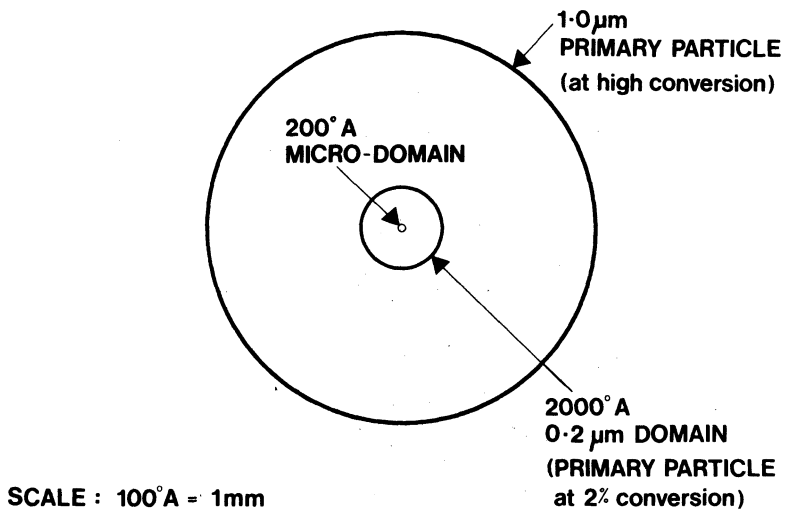


Fig. 5 Scale model of PVC sub-microscopic structure.

CLASSIFICATION OF PVC MORPHOLOGY

It is clear from the previous section that PVC morphology covers a wide variety of size scales and for the purposes of discussion in this paper three levels are identified. Macro-scopic will refer to all size entities above $10\ \mu\text{m}$, micro-scopic covers the range $10\ \mu\text{m}$ - $0.1\ \mu\text{m}$ and sub-microscopic below $0.1\ \mu\text{m}$.

The role of temperature in the control of PVC grain morphology is often ignored or not defined in papers on this subject. Initially, this paper considers the morphology resulting from polymerisations conducted at 50°C where high K-value polymer is produced. Later, the effect of higher polymerisation temperatures in producing a more coherent structure of lower porosity is also reviewed.

Macro-Morphology of suspension polymerised PVC

In the suspension polymerisation of VCM the bulk monomer phase is dispersed in water by vigorous agitation and the droplets produced are stabilised against coalescence by the presence of a granulating agent or protective colloid. An immense variety of agitation regimes and different protective colloid combinations are possible but in essence three main mechanisms are possible, Fig. 6.

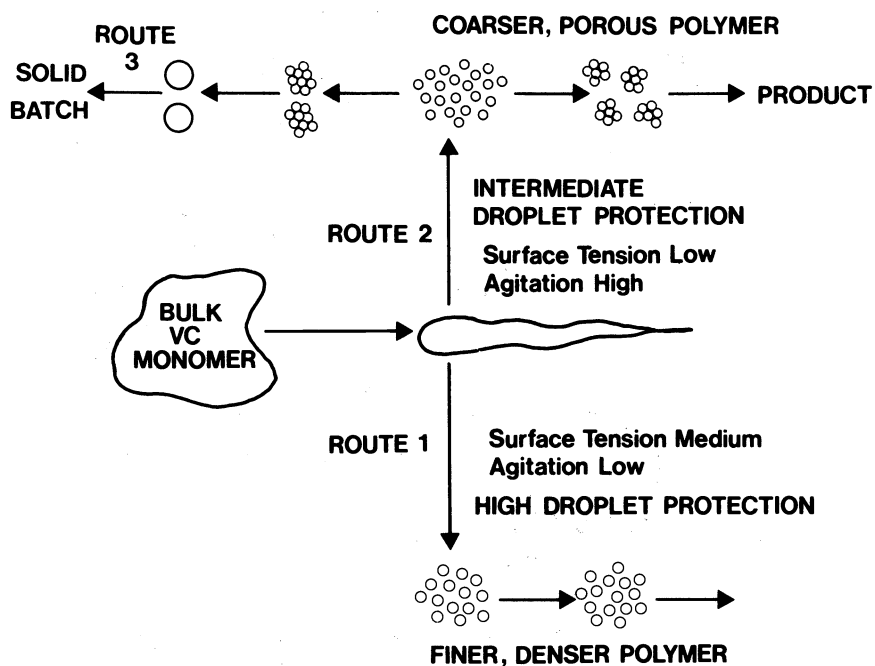


Fig. 6 Schematic diagram of the effect of VCM droplet stability on the macro-mechanism of polymerisation.

Route 1. The monomer droplets can be extremely well protected and once formed are completely stable against coalescence and survive throughout the whole polymerisation process as individual droplets to give rise to an essentially spherical, fairly fine sub-grain of low porosity.

Route 2. An intermediate level of protection is applied so that the droplets undergo controlled coalescence during the polymerisation to give rise to a more irregular shaped grain of intermediate size and higher porosity. A very wide variety of end products can be produced by subtle variations in the level of protection/time and extent of coalescence.

Route 3. Inadequate protection is given in which case the monomer droplets coalesce freely at low conversion to produce the PVC manufacturer's nightmare - one grain the same size as the reactor.

Most commercial polymers are produced by route 2 with speciality resins, eg paste filler, gramophone record, etc, by route 1.

The degree of protection afforded to the monomer droplets depends on the type and concentration of the protective colloid used. The level of agitation depends on stirrer speed, agitator type, size and shape and arrangement of baffles. In essence, the higher the level of agitation the smaller the VCM droplets and the greater the surface area to be protected. Different types of protective colloid have a considerable influence on both droplet formation as well as the droplet protection stage. As a result the macro-scale shape of PVC grains is quite varied, Fig. 7. A useful classification of the range of possible structures was presented by Tregan and Bonnemayne, Fig. 8, (3). If a comparison of Figs. 6 and 7/8 is made it is clear that the suspension polymers on the left hand side of the above chart are made by a Route 1 process, whereas the centre and right hand side polymers by intermediate and route 2 mechanisms respectively.

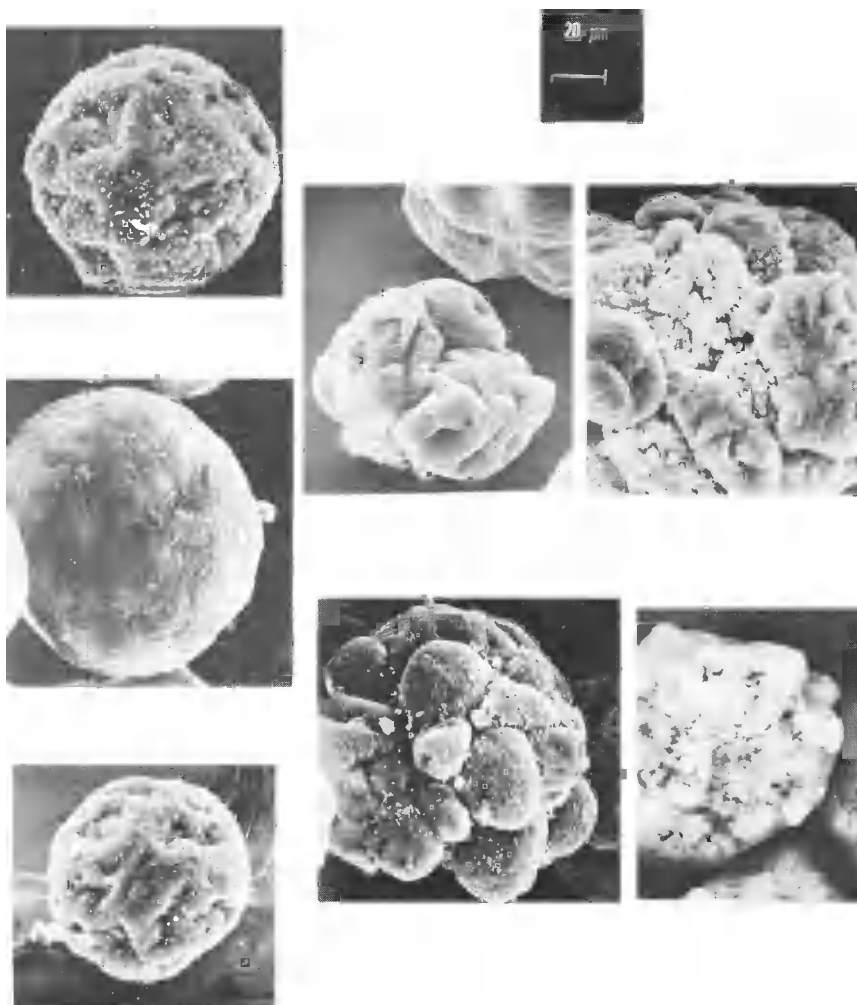


Fig. 7 Typical variations in PVC grain macro-morphology.

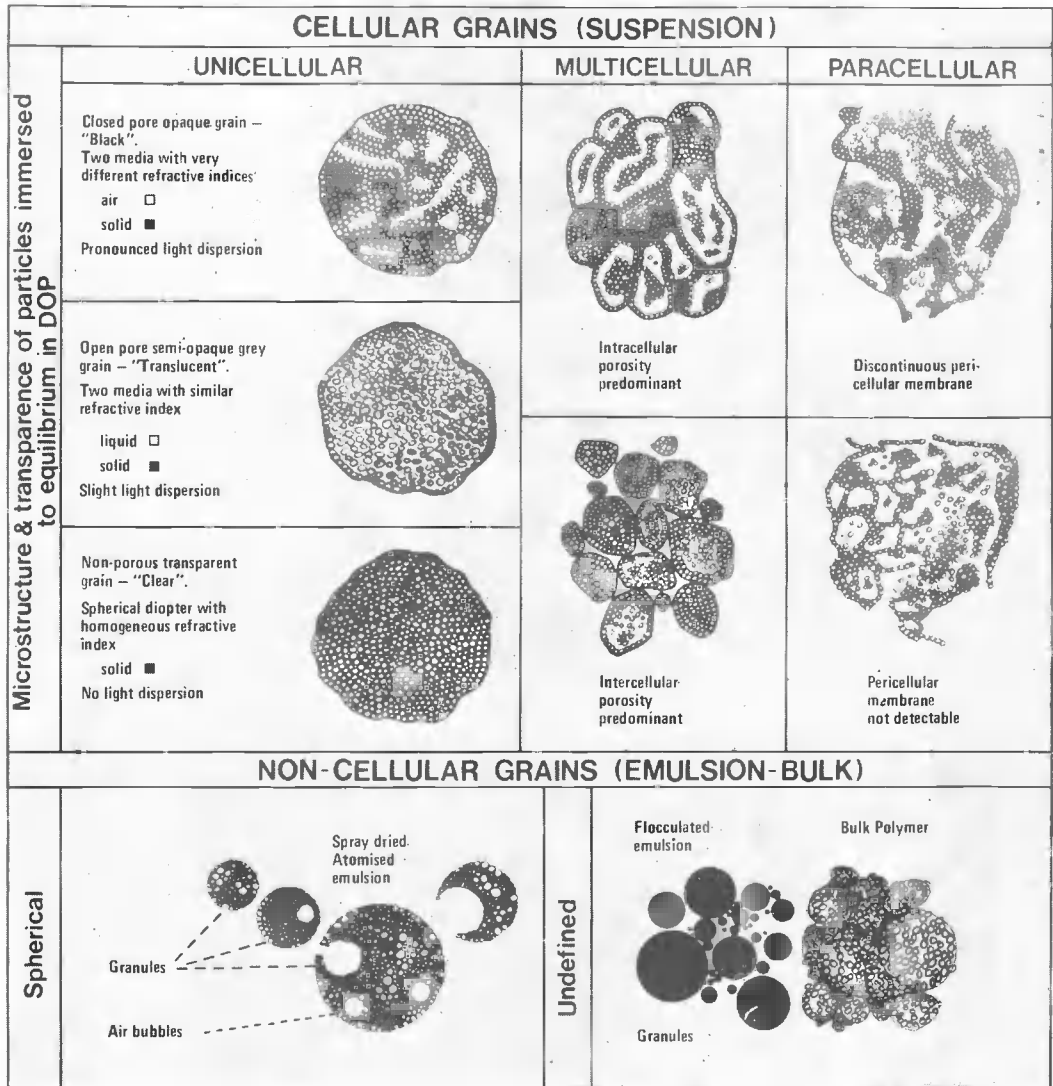


Fig. 8 Classification of PVC grains.

A simple technique for studying the macro-structure of suspension PVC clarifies the classification of the grains on the left hand side of Fig. 8. A sample of the polymer is immersed in di-alkyl (7-9) phthalate (DAP) plasticiser on a microscope slide and after equilibration is viewed at low magnification (100x) by transmitted light. The choice of a plasticiser with a close refractive index to PVC (DAP = 1.519, PVC = 1.542) allows clear observation of the internal morphology of each grain, Fig. 9. This simple test allows PVC grains to be separated into three basic structures depending on their optical appearance:

- (i) "Blacks" - grains containing closed pores which are not connected to the surface and are not fully wetted by plasticiser leaving air pockets within the grain, giving two regions of very marked refractive index difference. Pronounced diffraction of the light rays at the PVC/air interface gives rise to "black" zones in the grain.
- (ii) "Transluents" - grains of high porosity where the latter is evenly distributed throughout the grain. Since the refractive index of the PVC and the DAP are similar only slight diffraction occurs giving the grains a "translucent" appearance.
- (iii) "Clears" - solid grains containing little or no porosity. Light rays are diffracted at the surface only since the refractive index of the grain interior is almost constant giving a "clear" appearance.

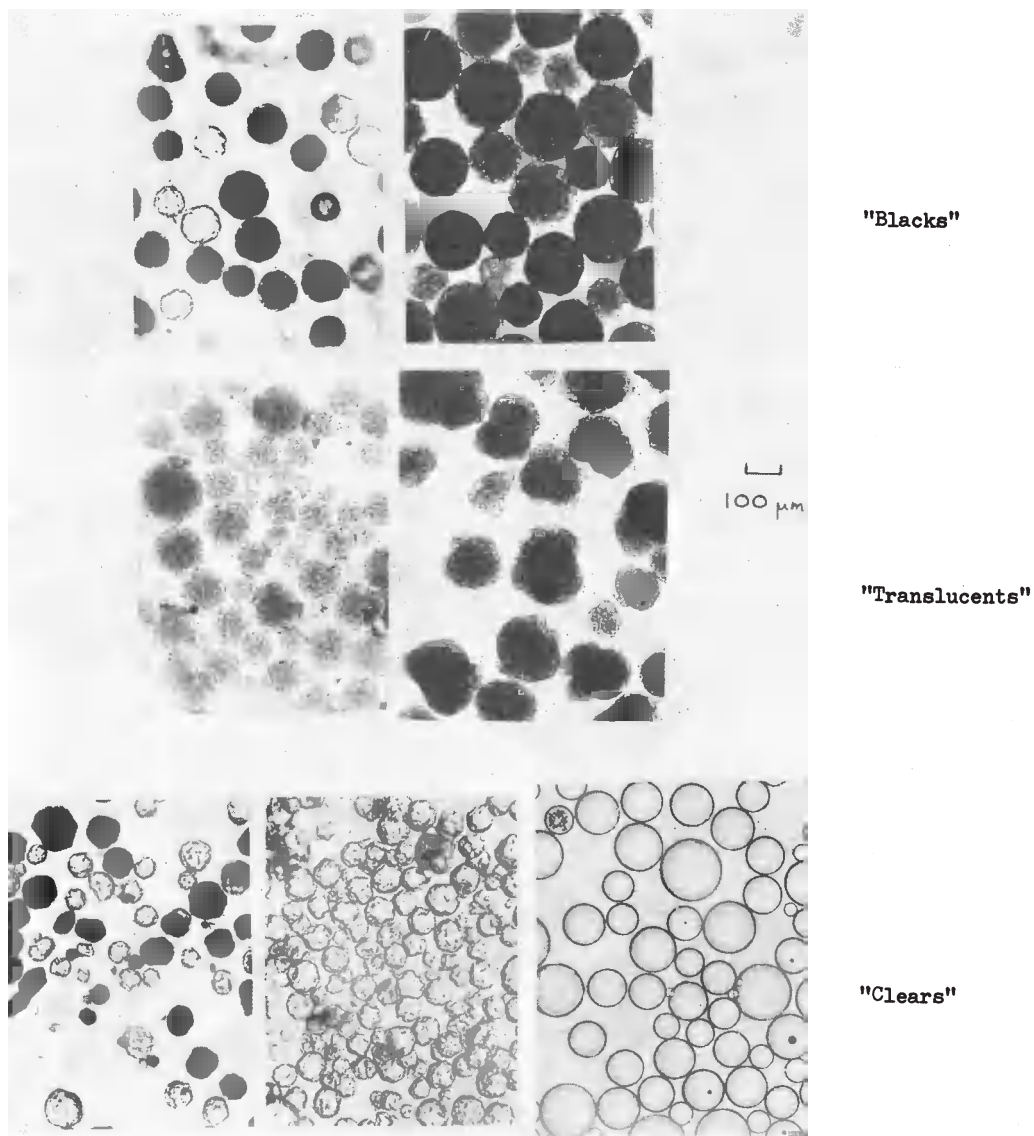


Fig. 9 Optical classification of PVC grains in DAP.

These three grain types can be produced in any of the classifications shown in Fig. 8, not just route 1 grains, but as the mechanism of polymerisation tends towards the route 2 type the translucent type is more typical, Fig. 9.

In order to understand how these structures are formed it is necessary to investigate the mechanism of polymerisation in a typical suspension system.

A well defined membrane around the droplets is seen to form at low conversion and this has been shown to be a PVA/PVC graft copolymer. As conversion rises this becomes more coherent, Fig. 10. Depending on the recipe used, varying levels of coalescence can now take place, see Fig. 6, over the range of conversion 5-15%. At about 30% conversion the membrane is quite strong and stable. During this time density changes are occurring within the droplet as monomer of SG 0.85 is converted to PVC SG 1.4.

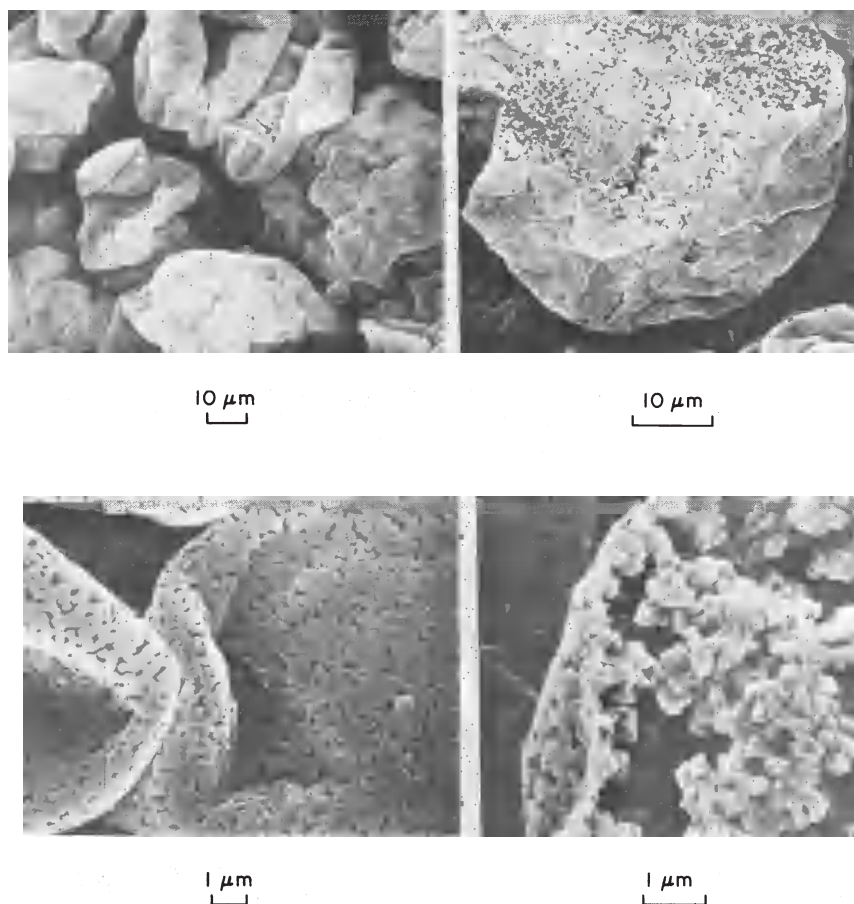


Fig. 10 Membrane formation at low conversion.

Around 65-70% conversion, most of the unreacted monomer is dissolved in the PVC and as polymerisation proceeds, the pressure within the grain falls and the grain collapses with folding and rupturing of the surface - accompanied by intrusion of water. This accounts for the wrinkled surface appearance of the PVC grains shown in Fig. 1 and some of the following micrographs. If samples of grains produced before 70% are examined before degassing of unreacted monomer a smooth surface is observed. As conversion rises further the extent of folding and rupturing of the grain increases slightly until the polymerisation is terminated by degassing un-reacted monomer. For commercial polymers this is usually in the range 80-95%.

As the conversion increases considerable changes in bulk polymer properties such as mean grain size and distribution, apparent density, packing density, powder flow, etc, can be related to the macro-structure changes, but some properties, eg surface area, porosity, vary appreciably, yet the changes seen on the macro-scale appear small. It is left to other levels of structure to provide an explanation.

Micro-scopie scale

While the macro scale changes involving droplet formation, coalescence, growth and collapse are taking place a series of similar changes on the micro-scopie scale are also being enacted in the monomer phase, Fig 11. Within the droplet the first formed PVC coagulates to form $0.2\ \mu\text{m}$ primary particles (domains) at an early stage, less than 2% conversion. The whole droplet turns cloudy as this phase separation step occurs with the interfacial region, a zone of particularly high activity.

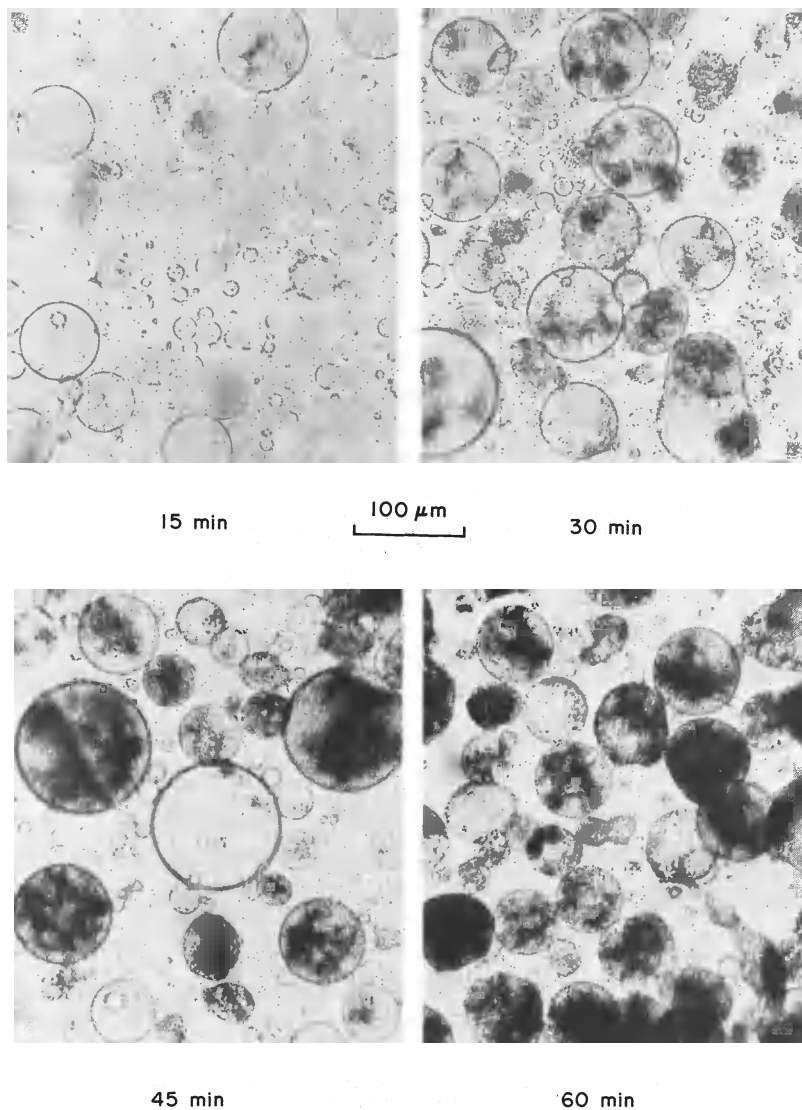


Fig. 11 Changes occurring in VCM droplets during the early stages of polymerisation

Graft copolymerisation of PVC on to the PVA protective colloid not only starts the process of forming the skin but begins to modify the nature of the interfacially adsorbed polymer, which lowers the covering power of the material and more is absorbed from the aqueous phase, Fig. 12.

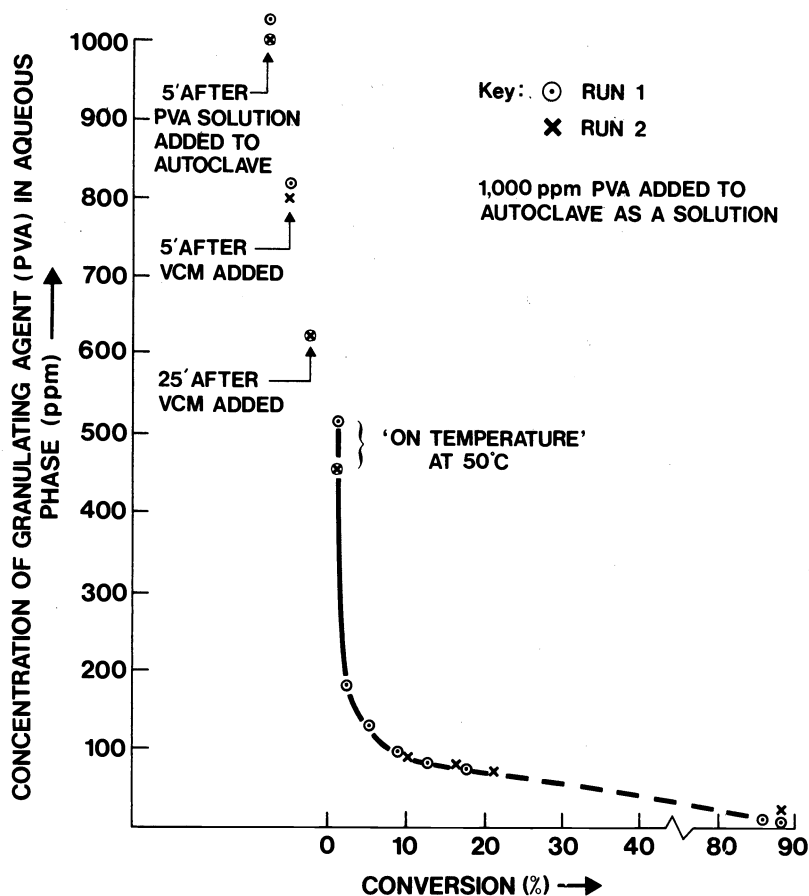


Fig. 12 Adsorption of granulating agent from the aqueous phase.

Although subjected to intense Brownian motion, the primary particles remain discrete and are stable and continue to grow. In the range 3-10% conversion they become unstable and flocculate to form close-packed agglomerates of 1-2 μm diameter. Due to the conditions prevailing at this time, different spacial packing arrangements of these agglomerates is possible and this step is perhaps the most important in defining final grain morphology. If the agglomerates pack loosely the final grain is porous whilst close packing results in a dense grain of low porosity, Fig. 13. Further polymerisation after this stage by surface deposition and internal growth of existing aggregates and their constituent primary particles produces a gradual increase in size to 2-10 μm respectively in the final product, together with an increase in intergrowth - the degree of coherency of the whole network structure. Both temperature and the level of agitation have a marked influence on grain structure. Our results show that as the level of agitation progresses from low to high the grain structure changes from a dense spherical to a porous irregular type with a corresponding increase in porosity, Fig. 14. Likewise polymerisation temperature is an important variable used in practice to control molecular weight but this too has a marked effect on grain porosity, Fig. 15.

Changes in the micro-scopic level of structure have a marked influence on virtually every type of polymer property. Surface area, porosity, plasticiser adsorption, gelation, are all controlled by the subtle changes in the micro-structure of the PVC. Yet again, some properties, eg hot plasticiser absorption, solvent dissolution, and visco-elastic melt properties cannot be explained in terms of micro-structure and an examination of sub-microscopic texture is required for an explanation.

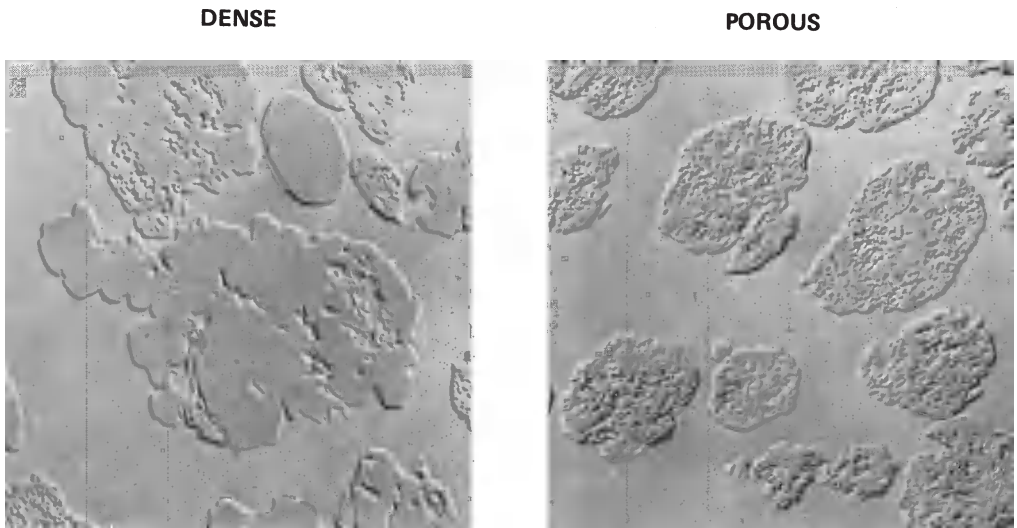


Fig. 13 Agglomerate packing in PVC grains
(Transmitted differential interference contrast microscopy).

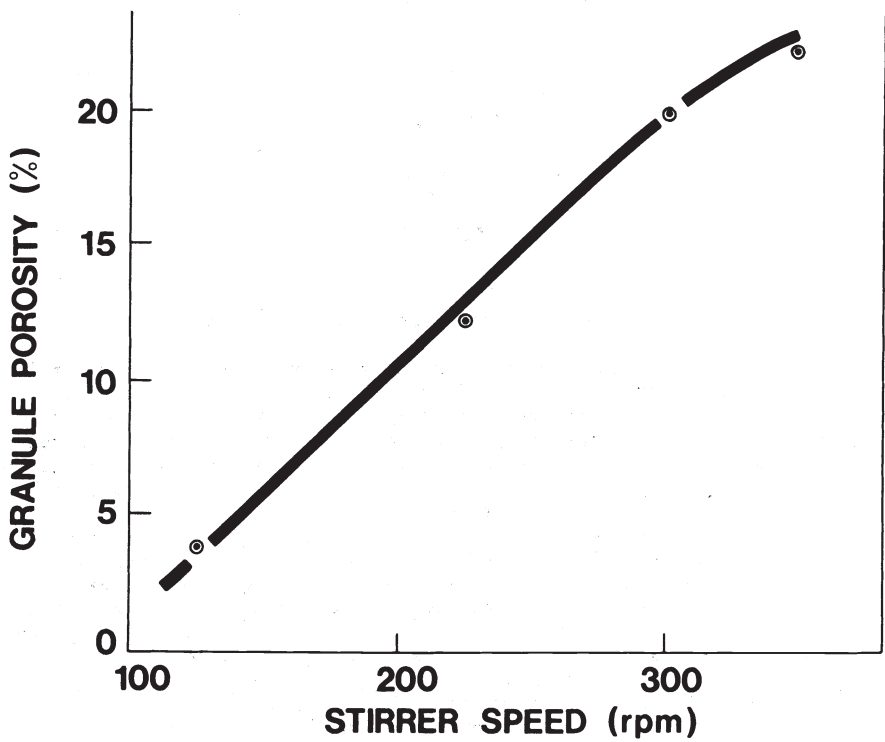


Fig. 14 Effect of agitation on grain porosity.

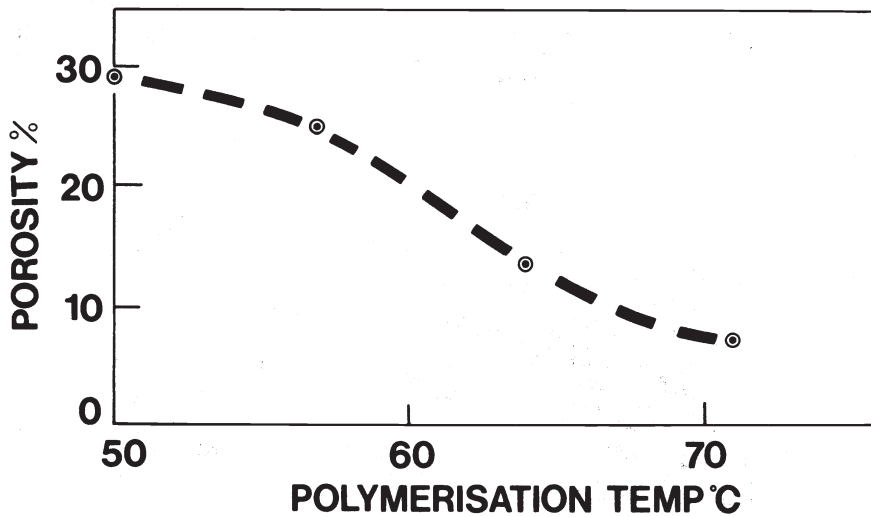


Fig. 15 Variation of net internal porosity with polymerisation temperature.

Sub-Microscopic scale

With the advent of a number of new techniques in recent years the macro- and micro-scopic morphology of PVC is now fairly well characterised, although much still needs to be done to understand and relate these morphological features to processing behaviour and in-service properties. Recently, more emphasis has been placed on characterising the sub-microscopic morphology of PVC. This is proving to be a very difficult field of study as one of the major problems, especially in unplasticised PVC, is simply resolving those structures present.

The main feature of interest at this scale of scrutiny is the micro-domain, some 100-200 Å in diameter, and the domain, an order of magnitude larger. The former was first identified in our laboratories in 1956 by Cobbold et al (5) when examining the replicated surface of an experimental polymer by transmission electron microscopy (TEM), Fig. 16. Since that time various literature references, for example, 6, 7, 8 and 9, have reported that entities of this size can be found in certain polymer samples.



TEM Replica 0.25μ

Fig. 16 Surface replica of micro domains.

During the course of further work in our laboratories in which bulk and suspension polymerisations were sampled at very low conversion clear evidence that the larger domain is produced by the aggregations of smaller sub-species was obtained, Fig. 17. Existence of particles (domains) in the size range 0.1-0.2 μm has also been reported by other workers using different techniques and appear to confirm that the domain (0.2 μm) is a real structural entity (6, 7, 8, 9 and 11).



0.1 μ

Fig. 17 Domains and microdomains in low conversion polymer.

Perhaps the best evidence for domains in plasticised PVC has been provided by Geil and co-workers at Case Western Reserve University (6 & 8). Using a freeze fracture technique micro-domains are clearly identified and are shown to increase in size with varying plasticiser content.

Following the mechanism of polymerisation proposed earlier it should be rewarding to examine material produced during the early stages of polymerisation in relation to sub-microscopic structure. If, as has been suggested, there is a crystalline nucleus or core associated with the basic micro-domain structure, or even a lamellar texture, then these feature should be easier to identify at the point of their morphogenesis at low conversion before additional growth and agglomeration takes place and obliterates the structure.

Using laser Raman spectroscopy on material isolated at about 2% conversion it is possible to show that this material produced at very low conversion is indeed more crystalline (12).

Small angle x-ray scattering (SAXS) measurements on PVC can be attributed to a two-phase super molecular structure of crystallites in an amorphous matrix. The arrangement of the crystallites can exhibit various degrees of order. When PVC is annealed under conditions that enhance crystallinity, the order is sufficient to produce a discrete, albeit broad, diffraction peak corresponding to spacings of about 100 Å (13). It is not possible to tell from SAXS alone whether this peak is the result of a stacked crystalline lamellar morphology or whether it is from semi-ordered arrays of spherical crystalline nodules. Electron microscope evidence tends to favour the nodular structure in which the 100 Å spacing is typical of the internodule distance. Without these annealing conditions, the crystallite arrangement remains disordered and probably consists of irregularly packed nodules with a distribution of sizes. The mean size of the nodules is of the order of 30 Å.

In addition to examining low conversion polymer, high conversion material has been examined both before and after processing.

In high conversion polymer samples 1 µm primary particles in 5 µm agglomerates are easily identified but not the other size species. After processing it is particularly interesting that in addition to these species the 0.1 µm domains are also seen. This suggests that the primary particle nucleus retains its original identity, even though it undergoes extensive growth with conversion (Fig. 5). It may suggest that the domain is the location for the more highly ordered material mentioned in (12) since the material examined was of this size range, but this is not fully proven at the present time.

OVERALL MORPHOLOGY OF SUSPENSION PVC AND POLYMER PROPERTIES

Although the various levels of morphology that are generated during polymerisation have been considered in detail from a structural viewpoint they do exert a major influence on all stages of manufacture and processing. Many aspects of the polymerisation process itself together with the polymer/isolation stages of degassing, dewatering and drying are directly related to the morphology of the polymer being produced. Also, all subsequent steps from bulk handling, through mixing, processing and shaping depend on the total grain morphology.

Unfortunately, space does not allow a review of the influence of all the morphology parameters identified earlier on the life history of a grain. Since we are dealing with an aggregated particulate system two parameters can be selected which are essential to its characterisation. One is the spacial arrangement of the primary particle agglomerates laid down at low conversion within each grain. Unfortunately, no test method can characterise the agglomerates in this way and instead an examination of the inverse structure, the pores between the agglomerates, gives a measure of this morphology, expressed as porosity. Secondly, the strength of the continuum of agglomerates. The latter depends on the degree of fusion of each primary particle within its own agglomerate and between agglomerates. As conversion increases the gradual fusing together of the primary particles in the agglomerate is called "intergrowth".

Porosity is measured by mercury intrusion porosimetry or cold plasticiser absorption and intergrowth by hot plasticiser absorption at 75°C and solvent treatment of sections.

If the mechanism of gelation of unplasticised PVC is examined (14), it is seen to involve four steps - compaction, densification, fusion and elongation. The rate determining step is the length of time it takes to achieve grain to grain fusion since shear cannot be transmitted until this stage is reached. Porosity is very important since the formulation additives must be removed from the surface of the grains so as to allow fusion to take place. The higher the level of porosity and greater the absorption of additives the faster is the rate of fusion and hence gelation. Intergrowth is also important since the strength of the continuum of agglomerates determines the rate of densification, but the effect is secondary to additive absorption and porosity.

In flexible applications a rapid and uniform rate of plasticiser absorption is necessary in the manufacture of dry blends. Porosity allows wetting of the external surfaces of the agglomerates but the rate determining step at elevated temperatures is how rapidly the PVC matrix is solvated and expands to absorb the remainder of the plasticiser. Low conversion polymers with low levels of intergrowth record particularly short dry-up times in this test. This test clearly shows that there are significant changes taking place as the conversion rises, particularly when pressure drop occurs and the polymerisation enters sub-saturation conditions.

CONCLUSIONS

From the evidence gained so far it is clear that the growth of PVC takes place through a series of interconnected aggregation steps which can be represented in the following scheme, Fig 18.

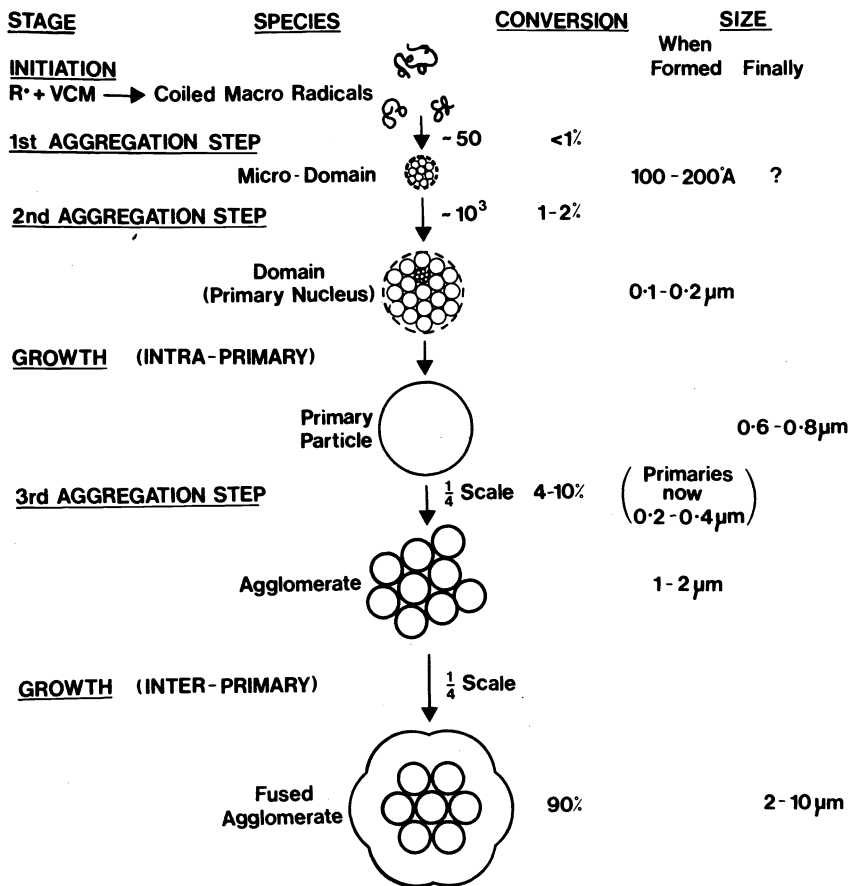


Fig. 18 Schematic representation of the mechanism of VCM polymerisation.

In the first instance the growing macro-radicals coil as they grow to give the first phase-separated species. The aggregation of some 50 of these to produce an unstable micro-domain (200 Å) gives us the first species which can be identified as a separate morphological unit. This in turn flocculates in much greater number (~ 1000) to produce the domain or primary particle nucleus. The next, and perhaps the most interesting step of all, is the growth of the primary particle, its flocculation into an agglomerate and the subsequent growth of the primary particles within an agglomerate. Some growth must inevitably occur in the VCM/PVC "gel-phase" since this contains a ready supply of monomer and some initiator "trapped" within its loose confines. One can envisage the growth of single chains building up the PVC network, but what of the mechanism on the VCM phase? In the early stages this is overwhelmingly predominant in volume and is the main source of initiator. Although it has been clearly established that no new primary particles form with conversion, is it possible that the growth element is the micro-domain? If so, some 50 chains would have to flocculate together to form this species before impinging on an existing primary particle surface and suffering capture. Certainly, if this were the mechanism one would expect to be able to identify micro-domains in high conversion polymer and this has yet to be achieved. Perhaps a smaller entity not yet identified is the growth species or are we left with the PVC macro molecule itself as the growth unit?

The subject of PVC micro- and sub-microscopic morphology has seen a tremendous advance in the last decade in terms of the ability to identify the species concerned. Perhaps the next few years will see the relationship between morphology and rheology and mechanical properties being clearly established. Progress is already being made. In a recent IUPAC working party (15) participants studied the effect of draw ratio on micro-morphology. The main conclusion of this work indicated that neither the 200 Å micro-domain nor the 0.2 µm domain structure is deformable of itself but that the connective tissue between the 0.2 µm domain is highly deformable. This evidence is consistent with the flow-unit of unplasticised PVC being an approximately spherical domain of about 0.2 µm diameter which is not itself deformable during processing. The internal structure of these units is composed of an agglomerate of structure on the 200 Å scale. It has been suggested that the 200 Å micro-domain is held together internally by "crystallinity" acting as cross links (10) but the connective tissue between the 0.1 µm domains is far less ordered and easily deformable. If progress is maintained at the present rate we should soon have answers to many of these questions.

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