

THE LIFE-CYCLE OF THE TWO PHASE SYSTEM IN VINYL CHLORIDE POLYMERISATION

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Abstract - Photon correlation spectroscopy (PCS) was used to obtain information on the state of the two phase system following phase separation in the very early stages of vinyl chloride polymerisation. Around a gel phase volume ratio of $\sim 10^{-3}$ the particle number appeared constant with the particles growing at constant rate until a sudden decrease in numbers set in at a certain particle size, indicating flocculation. A simple mathematical model is given to account for the observations. From this work and earlier studies a scheme is proposed for the complete life-cycle of the two phase system.

INTRODUCTION

Porosity is one of the commercially most important properties of suspension PVC. It is a term intended to cover the proportion of void space inside a PVC granule and a description of the shape of this free space. While the volume fraction is relatively easy to measure, to give a significant description of the shape of the void space is a task of daunting difficulty. Certain averages can be measured, they are of doubtful value however if the general pattern of the shapes to be characterised is not known. The void space is that part of the volume of a granule which is not taken up by polymer; if one understands the spatial patterns formed by the growing polymer then the morphology of the void space can be understood because it is complementary to the morphology of the polymer. It is for this reason that so much emphasis is put on the study of morphogenesis during the polymerisation.

Morphogenesis in the VC/PVC system can be described as a combination of three processes:

1. Phase separation of swollen polymer gel particles from the liquid monomer
2. Multiple aggregation of the gel particles
3. Growth of the gel, in whatever state of aggregation, by polymerisation.

These processes going on simultaneously and interacting with each other govern the life-cycle of the two phase system from its birth in the initial phase separation of the first polymer gel particles to its ossification, when at around 35-40% space filling the clusters formed from the multiple aggregation of gel particles lock into a contiguous network or skeleton spanning the space inside the granule.

The description of the early stages of the life-cycle of this two phase system is a task for colloid science because of the size and the types of interaction of the gel particles. It is however somewhat off the main stream of activities of most colloid science laboratories because of the experimental difficulties of handling the toxic liquid monomer.

A few a priori statements about the gel phase will define our point of departure in this work.

1. The polymer gel phase is expected to appear as "basic" particles the size of which is determined by the lifespan of the kinetic chain. (For polymerisation kinetics see Ref. 1). Each initiator decomposition step produces two radicals which by transfer to monomer generate about 20 polymer chains each. Because the transfer step is not longer than the intermolecular distance in the liquid, the 20 polymer molecules can produce one single coil equivalent to a molecule of ~ 20 times the chain length. Such a coil with an equivalent molecular weight of say $20 \times 62500 = 1.25 \times 10^6$ (DP = 1000 for each individual chain) has a mass of $\sim 2.1 \times 10^{-18}$ g polymer, or 3×10^{-18} g gel when swollen by monomer (Flory interaction parameter ~ 1). (2)
2. The diameter of a spherical gel particle of that mass is ~ 18 nm. At a rate of increase

of the gel volume fraction of $\sim 1 \times 10^{-6} \text{ s}^{-1}$ the number of basic particles of that maximum size appearing will be $\sim 0.33 \times 10^{12} \text{ cm}^{-3} \text{ s}^{-1}$ and their average distance from each other $\sim 1.45 \times 10^{-4} \text{ cm}$. The basic particles may well be smaller than the maximum size deduced here, and then appear at shorter distances from each other. No direct experimental evidence is available for their presence. Their existence, however transient, follows as an inevitable conclusion from the Flory interaction parameter of the VC/PVC system, which limits the solubility of polymer in monomer to polymer chains of ~ 10 monomer segments (3) and the rate of polymerisation. Because of these constraints the mechanism of polymer colloid formation adopted here is slightly at variance with the one proposed by Fitch, and discussed by Speirs.(8) We consider that the number of polymer chains which are captured directly by existing particles is limited by the very short critical chain length of ~ 10 segments to chains initiated within a monomer layer of thickness not more than 2-3 times the critical chain length (say $< 4 \text{ nm}$) around existing gel particles. This is a negligibly small fraction of the monomer in the early stages of polymerisation.

3. The first particles that can be observed by any technique are the "primary" particles, with diameter from 80 nm upwards. They carry negative electrostatic charges and can form stable colloid suspensions in liquid monomer (4). The number of charges per primary particle is small, < 40 .

The purpose of the work reported here was to investigate by experiment the behaviour of colloid gel particle suspensions as they first appear on polymerisation and at the same time to develop a model of the behaviour of these suspensions based on what we believe are true statements given above about basic and primary particles in the VC/PVC system and the accepted tenets of colloid science.

EXPERIMENTAL

Using the PCS technique it is not possible to follow precipitation polymerisation as it occurs within suspended monomer droplets. However, the same colloidal events occur during bulk polymerisation, which is experimentally easier to observe. VCM was condensed into cylindrical glass tubes of internal diameter 2.5 mm from a stock contained as a vapour in the storage bulb of a vacuum frame. This monomer had been freed from inerts but no attempt was made to remove residual water vapour. A sample volume of 0.15 cm^3 monomer contained di-lauroyl peroxide as initiator at a concentration of 0.1% w/v on monomer. The tubes containing monomer and initiator, frozen to liquid nitrogen temperature, were sealed by a flame, so that the tubes were short enough to be completely immersed in a water bath on the spectrometer table.

The incident light source of the PCS spectrometer was provided by a 5mW helium/neon laser which has a wavelength of 632.8 nm. The photomultiplier was set at an angle of 90° to the incident beam. The photocurrent was analysed using a 48-channel digital correlator (Malvern Instruments). In addition to measuring the light scattered from a polymerising sample, the transmitted light intensity was simultaneously measured using a photogenerative cell. The output voltage was recorded by a chart recorder. Monomer samples were placed at the centre of the spectrometer table in a water bath which maintained the pre-set polymerisation temperature to $\pm 0.01^\circ\text{C}$, and PCS measurements were made as often as possible after initiation of polymerisation.

Full experimental details of sample preparation and the interpretation of both photon correlation and transmittance data will be reported elsewhere (Ref. 5).

RESULTS

When monochromatic light is scattered by a dispersion of particles, the scattered light has a Lorentzian frequency distribution, the line width of which is related to the diffusion coefficient of the dispersed particles. The Malvern instrument makes a Fourier-transform of the frequency distribution to produce a time autocorrelation function from which the translational diffusion coefficient and hence the size of the particles can be determined. By applying standard Mie theory to the particle size and transmittance data, the particle number per unit volume was also calculated. By combining particle size data, obtained by PCS measurements, with particle number calculated from simultaneous transmittance measurements the volume fraction of swollen polymer (conversion) as a function of time, and hence the kinetics of polymerisation in its early stages were obtained. The only physical data for VCM and PVC required in calculations were the viscosity of the monomer, the refractive index of the monomer and the refractive index of the precipitated polymer in the temperature range of the polymerisations. The viscosity and polymer refractive index data were obtained from the literature (Ref. 6) and measurements were made of the refractive index of the monomer as a function of temperature at wavelength 632.8 nm (Ref.7). Two assumptions were made in the calculations from the light scattering measurements, firstly that the

growing primary particles in the monomer phase were monodisperse. Studies on polymer particles obtained at these low conversions by electron microscopy in this and other work (Ref.8) suggest that the coefficient of variation of the distribution is indeed small. The second assumption was made in calculating the refractive index of primary particles. Here it was assumed that the swelling of the primary particles by monomer is given by the equilibrium swelling ratio of fully polymerised PVC as given by Berens (Ref.9) (the phase volume ratio of polymer to monomer is 2:1). In making measurements on a polymerising system, it is important that the system remains relatively unchanged during the period of measurement and hence VCM polymerisations with slow kinetics yielded the most reliable information using the PCS technique. The data from measurements shown in Figure 1 are for a polymerisation carried out at 35°C, the lowest temperature for which data were obtained. A number of features immediately emerge.

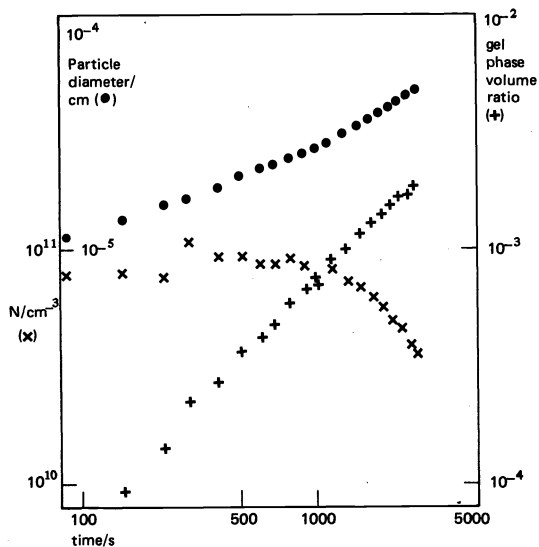


Fig. 1. PCS data for vinylchloride polymerisation at 35°C. Particle diameter, particle number and gel phase volume ratio are shown as functions of time in logarithmic representation.

The conversion from monomer to polymer in the early stages of polymerisation obeys first order kinetics and this was observed for all polymerisations studied in the temperature range 35°-55°C. The first particles which can be detected by PCS measurements are already primary particles. Repeated attempts to detect basic particles which have diameter 5-10 nm at the start of polymerisation met with no success, suggesting that their life time is very short and that coagulation of basic particles to produce primary particles occurs during the first 30 s of polymerisation. The data in Fig. 1 also show that as primary particle size increases, the particle number remains constant for the first 20 minutes of polymerisation, a key observation for discussing the mechanism of colloidal stability of primary particles.

The onset of flocculation of primary particles can also be seen in Fig. 1. The linear decrease in particle number is accompanied by a faster increase in particle size. Similar features were observed for polymerisation at all temperatures studied.

The conversion to which polymerisation can proceed before PCS measurements become unreliable depends on the particle size, particle number, refractive index ratio of the dispersed phase to the dispersion medium and the cell pathlength. The translational diffusion coefficient can be obtained from PCS measurements only when light reaching the photomultiplier is scattered just once. In practice for monomer swollen PVC particles in VCM, using cells of pathlength 2.5 mm, it was found that data could be interpreted provided that the transmittance remained >0.15. The lowest transmittance for data shown in Fig. 1 is ~0.2, giving confidence that the changes observed are not an artifact of the technique.

Data for polymerisation at higher temperature are shown in Table 1. An Arrhenius plot of log polymerisation rate constant against reciprocal of the absolute temperature is shown in Fig. 2. The slope of the line gives a value for the activation energy for VCM polymeris-

ation of $87 + 3 \text{ kJ mole}^{-1}$, which is close to previously quoted values of Norrish and Bengough (Ref. 10).

TABLE 1. Summary of results

Temp (°C)	Polymerisation rate constant $\times 10^6 \text{ (s}^{-1}\text{)}$	Equilibrium number of primaries $\times 10^{11} \text{ (cm}^{-3}\text{)}$	Stability ratio (W/kT)	Critical volume fraction for coagulation (10^{-3})	Critical diameter of primary at coagulation $\times 10^4 \text{ (cm)}$
35	0.77	0.85	7.4	0.8	0.28
40.2	1.50	1.5	7.2	1.4	0.28
45.3	2.02	1.4	7.2	2.0	0.3
50	3.80	1.7	8.0	1.2	0.25
50.6	3.67	3.2	6.8	2.0	0.24
55.1	5.48	2.5	7.9	1.4	0.24
55.1	6.52	3.5	7.3	2.3	0.24

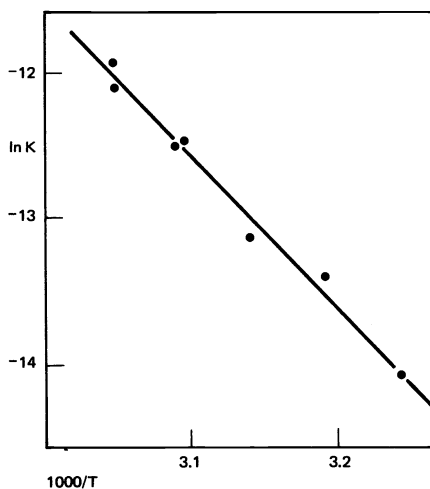


Fig. 2. Arrhenius plot

Despite the extreme care taken to prepare monomer samples for polymerisation, the differences in polymerisation rate and the equilibrium number of primary particles obtained in duplicate experiments at 50°C and 55°C clearly indicate the problems in obtaining reproducibility of results for such small-scale polymerisations. Although the glass tubes were thoroughly cleaned before use, the high surface to volume ratio of the tubes suggests the glass surface as the principal source of monomer contaminants.

DISCUSSION

Before attempting to interpret the experimental results presented in the preceding section we want to sketch the outlines of the colloid events one would expect a priori to take place in a two phase system in which a new gel phase appears as a flux of small (basic) particles. We shall then discuss how expectation rhymes with observation.

Small particles in the absence of any mechanism to give them colloid stability will flocculate or aggregate at a rate proportional to the square of their number in unit volume.

$$n' = -K_{flb} n^2 \quad (1)$$

The basic particles appear at a constant rate

$$n' = K_b \quad (2)$$

After some time a steady state will be approached in which the number of particles in unit volume is constant.

The number of basic particles at any time is obtained by combining equations 1 and 2 and integrating

$$n(t) = K_b \frac{1}{2} K_{flb}^{-\frac{1}{2}} \tanh\left(t K_b^{\frac{1}{2}} K_{flb}^{\frac{1}{2}}\right) \quad (3)$$

Assume that the reactions giving rise to the flux of basic particles produce initially some charged species eg by elimination of a trace amount of oxygen from the system, and that this charge is associated with some basic particles. If the number concentration of the charged species is small compared to the number concentration of basic particles, this charge will not contribute to the colloid stability of the basics.

The aggregation of basic particles produces primary particles, the first observable entities of the new monomer swollen polymer gel phase. If they are not stabilised in the colloid sense they will flocculate according to a law similar to equation 1. If they have some colloid stability resulting eg from the charged species just mentioned flocculation will be delayed and its rate reduced according to

$$N' = -K_{flp} N'^2 \exp\left(-\frac{W}{kT}\right) \quad (4)$$

where W is the energy barrier that has to be overcome before two particles can collide, a measure of the amount of the colloid stability of the primary particles.

Polymerisation increases the volume fraction of the gel phase by

- i phase separation of basic particles from the monomer
- ii polymerisation inside the gel phase.

The size and life span of free basic particles are probably so small that the likelihood of an active radical arising within the particle volume can be neglected. Therefore basic particles are taken to have constant size given by the parameters of the reaction mechanism as set out in the introduction.

By contrast primary particles and higher aggregates do grow:

- i by accretion of new basic particles onto their surface
- ii by polymerisation inside the gel phase.

The relative importance of these two growth mechanisms will depend on the volume ratio of the two phases, on the partition of initiators between them and on the ease with which radicals pass the phase boundary in either direction. At gel phase volume ratios of 10^{-3} or less gel phase polymerisation is likely to play but a minor role while accretion of basic particles dominates the growth process.

If the growth of colloiddally stable primary particles proceeds by the capture of basics then the basics captured by the primaries are prevented by their capture from colliding with other basics to form new primaries. The world line of a freshly phase separated basic particle therefore ends either in a doublet soon to become a critical nucleus of a few basics which will grow into a primary particle, or on the surface of an already existing primary. There is no third possibility, the probabilities of these two alternative world lines must add up to one. An equivalent way of expressing this conclusion is the statement that the flux of polymer through basics into new primaries and the flux of polymer through basics into growing primaries together amount to the total flux

$$vn'_N + vn'_V = vn'_{tot} = VN' + NV' = K_{pol} \quad \text{and} \quad (5a)$$

$$VN + vn = tK_{pol} \quad (5b)$$

It seems reasonable to assume that the ratio of the probabilities of the two world lines open to freshly formed basic particles will be the ratio of the collision cross sections of basics and primaries.

$$VN'/NV' = \text{RCCS (Ratio of Collision Cross Sections)} \quad (6)$$

This assumption is a very crude approximation to reality because it treats everything below the critical nucleus size as a basic particle and everything greater as a primary, and

assigns significant dimensions and numbers to both populations. It is adequate for our present purpose. A much more ambitious approach to the coagulation problem was published recently (11).

By expressing in equation 6 all variables relating to primary particles in terms of \bar{R} and D and integrating the resulting expression one has:

$$-4r^2 d \frac{R^{*-2}}{R} = D^{-2} + C \quad (7)$$

Inspection of equation 7 shows, as expected, that with increasing size \bar{R} of the colloiddally stable primary particles, their number expressed by the inter-particle distance D (remember $N = D^{-3}$) tends to level off. The integration constant C can be evaluated by considering the two extreme conditions of the polymerisation process: the beginning with D large and $R \rightarrow R_0$ small and its progress towards R large and $D \rightarrow D_{eq}$ small

$$C = -4r^2 d \frac{R_0^{*-2}}{R_0} = -D_{eq}^{-2} \quad (8)$$

This gives a relation between the critical nucleus size R_0 and the equilibrium particle number or interparticle distance D_{eq} . If one expresses the integration constant C in terms of the critical cluster size, solves equation 7 for D , substitutes this into the polymerisation equation 5b and uses equation 3 to express $n(t)$ one finds

$$[a^{-2} r^2 (R+r)^{-2}]^{\frac{3}{2}} R^3 \pi \cdot 32/3 + v = K_{pol} t [K_b^{\frac{1}{2}} K_{flb}^{-\frac{1}{2}} \tanh(t K_b^{\frac{1}{2}} K_{flb}^{\frac{1}{2}})]^{-1} \quad (9)$$

which relates R directly to t and known parameters of the system. By tabulating the left hand side as function of R and the right hand side as function of t and drawing the appropriate graphs, corresponding values of R and t can be found. From R one obtains N through

$$[4d^{-2} \{a^{-2} r^2 (R+r)^{-2}\}]^{\frac{3}{2}} = N \quad (10)$$

which is an intermediate result in the derivation of equation 9.

$R(t)$ and $N(t)$ are functions derived from colloid theory and our view of the physics and chemistry of the VC/PVC system on its way towards a gel phase volume ratio of $\sim 10^{-3}$. We expect these functions to give a fair description of the behaviour of real systems.

By using the rate of polymerisation found in the PCS measurement at 35°C and taking basic particles of volume 10^{-18} cm^3 we have calculated $n(t)$ from equation 3. We take the particle number concentration measured by PCS in the plateau to give us D_{eq} , the integration constant and the critical nucleus size by equation 8. This latter turns out to be ~ 1.5 times the diameter of a basic particle corresponding to a critical nucleus consisting of 3-4 basics.

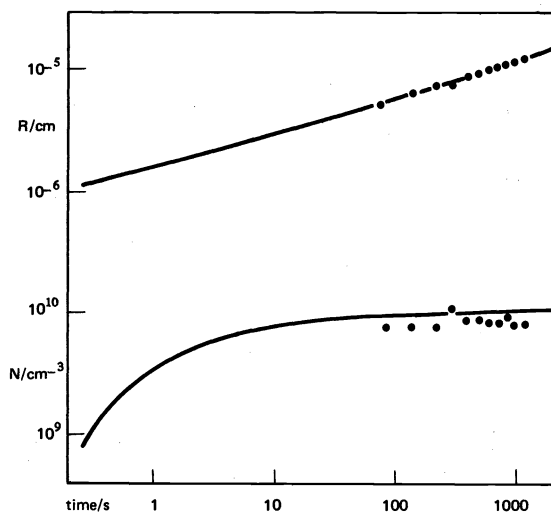


Fig. 3. Calculated functions $R(t)$ and $N(t)$ for polymerisation at 35°C (continuous lines) and experimental data (dots).

With the integration constant and the rate of polymerisation we have related equation 9 to the experimental conditions prevailing at 35°C. The resulting functions $R(t)$ and $N(t)$ are shown on a log-log plot on Fig. 3. The relevant PCS data are also indicated. The fair agreement between expectation and observation vindicates our assumptions.

For higher temperatures we would expect somewhat larger critical nucleus sizes, hence more and smaller primaries. This trend is borne out by the data in Table 1. Because of the increasing noise in the higher temperature data we did not do detailed model calculations for these runs.

The mechanism proposed for the formation and growth of primary particles is based on their colloid stability over part of their life-cycle. It has been shown beyond reasonable doubt that the colloid stability of primary particles arises from electrostatic charges (12, 4, 8). The sudden onset of flocculation of primaries at a critical size and concentration is discussed in great detail by Speirs who considers multiparticle interactions as studied by Albers and Overbeek (14) which are important in low dielectric constant media. Speirs calculations show the critical dependence of colloid stability on particle size at constant particle charge. His prediction is confirmed by the sharp onset of flocculation found in all PCS measurements and the remarkable constancy of the observed stability ratios W .

What is less clear is the origin, the nature and the location of the charge within the particles. The suggestion made by us (15) i.e. the adsorption of Cl^- and OH^- at the gel/monomer interface, whilst reasonable, does not lead to any prediction that could be tested. Melt flow studies (16) suggest that a non-deformable roughly spherical domain of ~ 100 nm diameter is the most likely flow unit in PVC. This is the diameter of the primary particles once their number is stabilised at a time when charge production as a side reaction to polymerisation is likely to have stopped. Assume that charges are not mobile but localised inside the gel, say onto double bonds left by dehydrochlorination of the polymer chains. It is then conceivable that a lattice of charges may be polarising the swollen polymer gel between the fixed charged lattice points, give rise to a domain of higher order and higher density than would exist in the absence of fixed charges. This suggestion of localised charges inside the primary particles is supported only by the circumstantial evidence of the melt flow studies. Colloid stability in a low dielectric medium is virtually independent of the location of the charge within the particle; we are not aware of any experimental technique to decide this question.

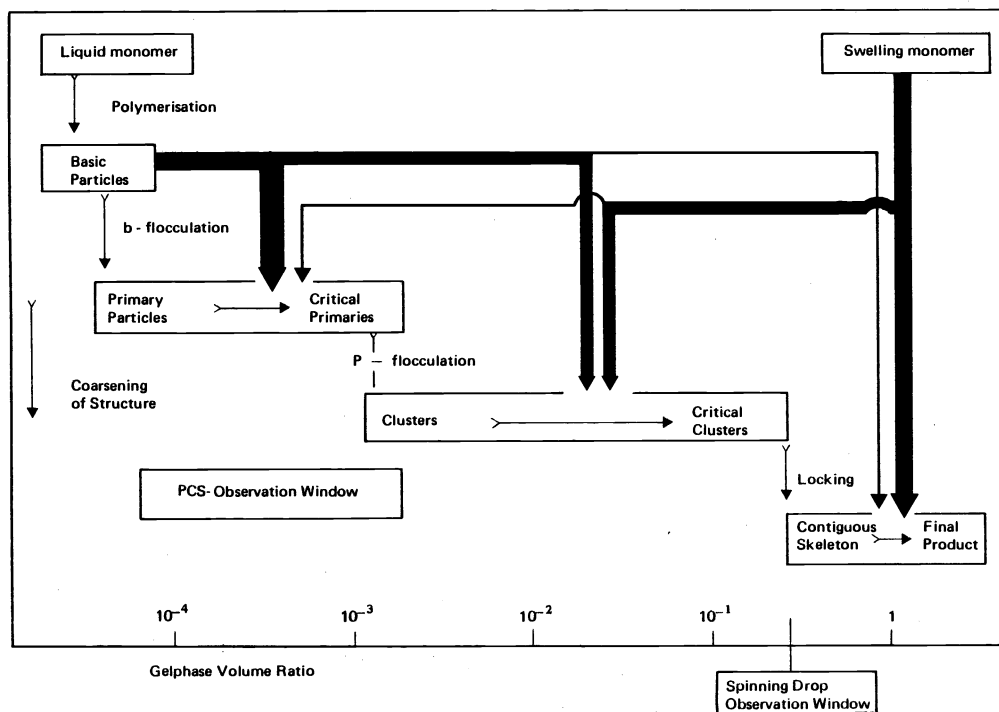


Fig. 4. The life-cycle of the two phase system in vinyl chloride polymerisation

The flocculation of primary particles leads to clusters (17). The cohesive strength of clusters depends on their internal contiguity, i.e. the number of contacts between particles, which reaches its first peak in the clusters of 13 particles (18). The stability of clusters against flocculation between themselves derives probably more from the fact that they can make only few small area contacts with each other, than from electrostatic repulsion. At

around 35% phase volume the clusters lose their mobility and lock into a contiguous particle network spanning the available volume.

Photon Correlation Spectroscopy has opened a window on the events occurring in the two-phase system in the very early stages of vinyl chloride polymerisation. Previous work with the spinning drop apparatus (17) gave a picture of the polymer phase at ~28% conversion. We all know the structure of the finished product. From these three sources of information it is now possible to put together a consistent sequence of events leading from the liquid monomer through a colloidal two-phase system to the porous solid polymer. A schematic illustration of these events is given in Fig. 4. Polymerisation proceeds from left to right on a logarithmic scale, coarsening of the gel phase by growth and flocculation from top to bottom. The observation windows opened by PCS and the spinning drop apparatus are indicated. The thickness of the arrows shows the relative importance of accretion and gel phase polymerisation. The scheme is a condensed statement of what we now believe are the facts in the life-cycle of the two-phase system in vinyl chloride polymerisation. It should help in formulating new questions.

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LIST OF MATHEMATICAL SYMBOLS

$$a = 2n_{eq}^{1/3} N_{eq}^{-1/3}$$

C = integration constant

d = centre to centre distance between basic particles

D = centre to centre distance between primary particles

k = Boltzmann constant

K = rate constants

n = number of basic particles in 1 cm³

N = number of primary particles in 1 cm³

r = radius of basic particle

R = radius of primary particle

*R = R + r

t = time

T = temperature

W = stability ratio

Subscripts:

b = basic particles

eq = equilibrium

fl = flocculation

p = primary particles

pol = polymerisation

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