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Studies of Nascent Polymer Morphology in Inertially Suspended Vinyl Chloride Drops

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ABSTRACT

A spinning drop apparatus was built for work at pressures up to 2 MPa and temperatures of 80°C. It was used to study the polymerization of inertially suspended vinyl chloride drops. The temperature dependence of the liquid vinyl chloride-water interface was measured in the temperature range 20-70°C and found to be linear. From the changes of the shape of polymerizing drops the locus of initiation could be deduced. If initiator is not adsorbed at the monomer-water interface, initiation is homogeneous throughout the volume of the drop. With interfacially adsorbed initiator, interfacial initiation occurs also. The morphogenesis of the precipitating polymer was studied by scanning electron microscopy of the polymer granules resulting from the polymerization of the suspended drops. The formation and aggregation of the primary polymer particles is discussed in terms of the theory of polymer colloids. Colloid stability of the nascent precipitating polymer is shown to be the dominant influence on aggregate formation.

1205

INTRODUCTION

Liquid vinyl chloride can be polymerized by a free-radical mechanism into a polymer insoluble in its monomer. The insoluble nascent polymer is swollen by about half its weight of monomer; it appears as a new phase in the form of discrete (primary) particles observable as a faint haze in the early stages of the reaction. After removing the swelling monomer the polymer particles are revealed by electron microscopy as discrete spheres or more or less agglomerated clusters or aggregates of spheres, depending upon the conversion at which polymerization was stopped. As polymerization nears completion, the particles or particle aggregates settle into a randomly close-packed structure which can be characterized by its porosity.

If the polymerization is carried out in an aqueous dispersion of monomer droplets, these will be transformed—perhaps after some coalescence—into porous granules. Porosity is one of the important properties of PVC; it has a reciprocal, mirror-image kind of relationship to the shapes and structure of the polymer inside the granules, i.e., to their internal morphology.

We have studied the development of internal morphology, morphogenesis, in nascent PVC by polymerizing individual, inertially suspended drops, by using scanning electron microscopy (SEM) to reveal the resulting morphology and attempting to relate these observations to the conditions of polymerization. In this paper the methods used in our study are reported, and some results are shown.

EXPERIMENTAL

Apparatus and Its Handling

A spinning drop apparatus was used for the inertial suspension of small (~ 0.05 g) vinyl chloride drops. It makes use of the axisymmetric conservative inertial force field that exists inside a confined volume of liquid rotating about an axis passing through the body of the liquid. The axis is at rest in an inertial frame of reference. In the steady state, i.e., when the circular frequency is constant and all parts of the incompressible, homogeneous liquid have come to rest in a corotating reference frame, the potential energy of any particle of the liquid will depend only on its distance from the axis of rotation, i.e., equipotentials will be concentric cylinders about that axis. Any material particle with a different density from that of the liquid will experience a force acting at right angles to the

axis of rotation, having a magnitude proportional to the density difference between the two materials and directed away from the axis if the material particle is denser than the liquid and towards it if lighter. If the confined body of liquid is contained in a closed cylinder rotating about its axis, a small volume of a nonmiscible fluid introduced into the cylinder will finish up as a flat ring on the cylinder wall or as an elongated drop in the cylinder axis, depending on its density relative to that of the supporting liquid. It is this latter situation which is used in the spinning drop apparatus for determining the interfacial tension between the drop and the supporting liquid. The shape of the drop depends only on the equilibrium between the inertial field and the interfacial tension, no contact with a third solid phase is involved. If the inertial forces acting on the drop are known, the interfacial tension can be calculated from the parameters of the shape of the drop.

Two recent publications [1, 2] give full accounts of the history and the theory of the spinning drop method of interfacial tension measurement. The equipment used and the mathematical treatment of data is discussed in detail.

Our equipment differs from that described by Torza and Wade in that it is designed to contain fluids under pressures up to 2 MPa. This is achieved by using as the rotating cylinder a thick-walled (6 mm) precision glass tube housed in a stainless steel cage, by dividing the volume of the tube in two compartments with a floating piston and by building a nonreturn mushroom valve into one of the two steel plugs closing the ends of the tube. These two steel plugs are attached to the cage surrounding the glass tube and act as shafts running in roller bearings. Magnetic coupling to a high speed motor provides a reasonably shake-free drive. A schematic drawing of the rotor assembly is shown in Fig. 1.

The function of the floating piston is to provide an air cushion to pressurize the liquid-filled compartment of the rotor. When the rotor is assembled, the floating piston is located at the valve end of the glass tube. The rotor assembly is now connected to a filling station (Fig. 2) and filled with water up to the desired pressure, thus moving the floating piston towards the closed end of the tube and compressing the air cushion. Any air bubbles remaining in the water are eliminated by releasing some water and refilling. The station is now switched to vinyl chloride and a small quantity is introduced, an operation which requires skill and patience to obtain the right quantity.

The rotor is now disconnected from the filling station and fixed on a vibration-free support (Fig. 3). The position of the rotor assembly in relation to the driving motor must guarantee the correct distance and alignment of the two halves of the magnetic coupling. The axis

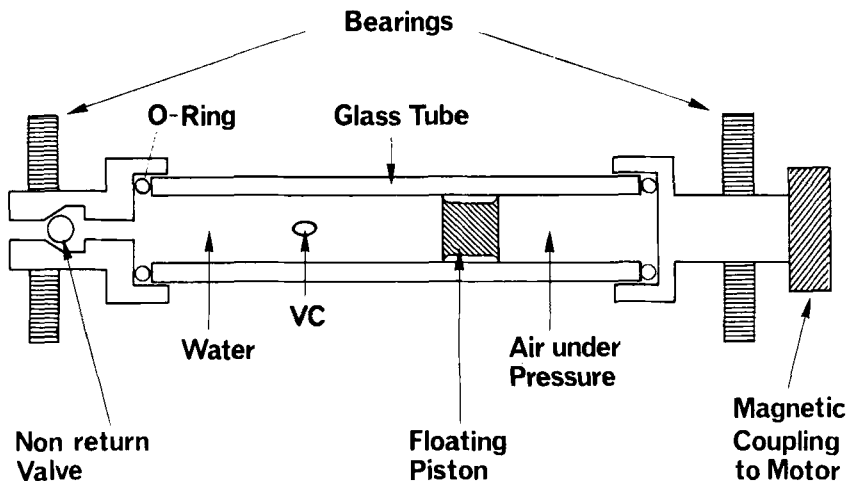


FIG. 1. Schematic drawing of spinning drop rotor assembly.

of rotation of the rotor should be within a few microradians from the horizontal to minimize gravitational effects. Even so, some precautions will have to be taken concerning angular frequency and drop-let size, as described by Torza [1]. The rotor assembly can be heated up to 80°C with a hot air blower and thermostatted by an on/off control on the blower to $\pm 0.5^{\circ}\text{C}$. The angular frequency is monitored by means of a magnetic probe sensing the passage of the teeth of a 60-tooth wheel on the motor shaft. It is displayed on a four-figure counter directly in revolutions per minute. For proper operation the read-out should be constant to within ± 1 digit at ~ 2000 rpm.

Interfacial Tension Measurements

The shape of the drop was determined from photographs taken with electronic flash on a modified old bellows camera. We used a 1:6.8/90 Schneider-Kreuznach Angulon lens and Polaroid-Land back working with an extension of about 50 cm. This gives a linear magnification factor from object to image of 5.10.

The electronic flash was used to illuminate an opaque white sheet of Perspex mounted vertically opposite the camera lens on the other side of the rotor. The flash was triggered by a silicon solar cell which received light across the rotor from a 4-V bulb. The triggering circuit was activated by opening the Synchro-Compur shutter

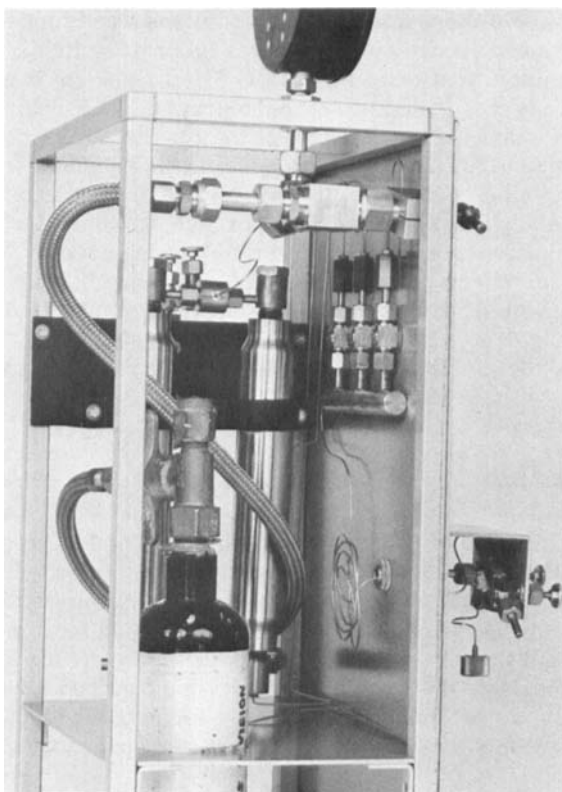


FIG. 2. Photograph of filling station.

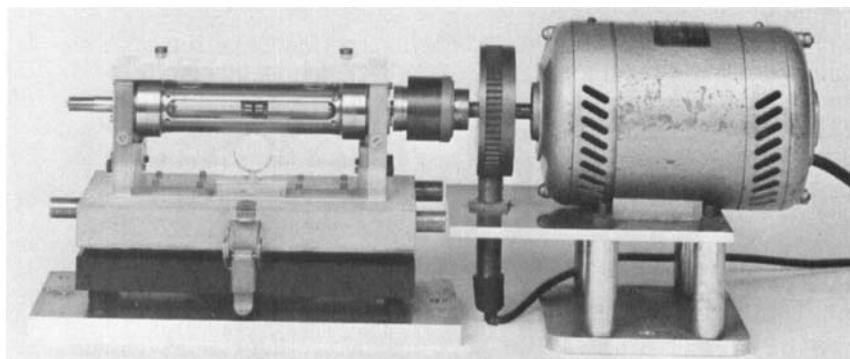


FIG. 3. Photograph of assembled spinning drop apparatus.

on the camera for a 0.5-sec exposure. The lens was stopped down to f32 to prevent interference by the general laboratory light.

The radial magnification of the water-filled glass rotor acting as a cylindrical lens was measured by photographing ball bearings of different sizes suspended in the axis of the tube; its value for the tube we used was 1.33. Interfacial tension measurements were carried out on "long" drops for which the ratio of length to width is greater than 4. The Vonnegut [3] approach was used for calculating interfacial tensions from the width of a long drop by $\gamma = 0.250\Delta\rho w^2 h^3$, where $\Delta\rho$ is the density difference between drop and supporting liquid, w is the angular frequency, and h is the half width of the long drop. Because of the great sensitivity of the results to errors in h , the pictures of drops were measured with a travelling microscope.

Polymerization

The main objective of this work was the study of PVC morphogenesis in polymerization under rigorously controlled conditions. All additives like initiators, colloid stabilizers, etc. needed for the polymerization runs, were introduced into the liquid monomer or the water held in their respective containers on the filling station. The liquids going into the spinning drop rotor contained all necessary ingredients, and no further additives were needed. The hot air blower was switched on only after a drop of the proper shape and stability was established.

Polymerization of inertially supported drops is limited to conversions for which the combined density of polymer and monomer inside the drop is less than that of the supporting liquid. In the vinyl chloride-water system the limiting density of $\sim 1 \text{ g/cm}^3$ is reached at $\sim 28\%$ conversion.

The internal morphology of the polymer granules produced in the spinning drop apparatus was studied by scanning electron microscope. Samples were prepared by cleaving the granules at liquid nitrogen temperature. The fracture surfaces were coated by evaporation with a first layer of carbon and a second layer of gold palladium. The total coating had a thickness of ca. $100\text{-}150 \times 10^{-10} \text{ m}$.

RESULTS

External Morphology: The Shape of the Spinning Drop

Interfacial Tension. Measurement of interfacial tension in the vinyl chloride-water system was not the prime objective of this

work. Such measurements are easy to perform but difficult to interpret because of the pronounced pressure dependence of the mutual solubility and hence relative density of the two phases and the consequent pressure dependence of the effective inertial force field. The shapes of vinyl chloride drops in water cannot be translated into true interfacial tensions without these data.

Bearing in mind these limitations, we can quote the temperature dependence of the apparent interfacial tension values σ^* , calculated with the "textbook" densities of the pure liquids in the temperature range 295-346° K.

$$d\sigma^*/dT = 0.028 \pm 0.002 \text{ mN/m} \quad (295\text{-}346^\circ \text{K})$$

$$\sigma^* = 32 \pm 1 \text{ mN/m} \quad (295^\circ \text{K})$$

$$\sigma^* - T(d\sigma^*/dT) = 40.2 \pm 1.6 \text{ mN/m} \quad (295\text{-}346^\circ \text{K})$$

The apparent linearity of the temperature dependence of σ^* , i.e., the constancy with temperature of the interfacial entropy, implies that the second temperature derivative of σ^* and hence the specific heat of the interface is zero. If this conclusion were true also for the real interfacial tension, it would mean that no ordering takes place at the interface. However, because of the uncertainty of the tension data this question cannot be decided.

Shrinkage on Polymerization. If one adds an initiator to the vinyl chloride drop and raises the temperature of the spinning tube, polymerization sets in and the drop begins to shrink. At ~28% conversion the density of the partially polymerized drop reaches that of water, and it is thrown out of the axis of the spinning tube.

One can deduce the load-bearing properties of the interface from the shape of the shrunken drop. A drop with a continuous skin of polymer resulting from interfacial initiation will deform differently from one whose interface is only a barrier against which nascent polymer particles are pushed in the centrifugal field.

If initiation (and hence particle nucleation) occurs homogeneously throughout the monomer, the particles will travel along the lines of force of the inertial field (~10 g at the equator of a 1-mm diameter drop) until they hit the interface, and depending on the friction between particle and interface, roll down hill to an equilibrium position. The added load around the equatorial regions of the drop/water interface causes a small increase in the equatorial radius. Consequently, one finds, after a polymerization proceeding in the homogeneous

nucleation mode, a particle heap in sedimentation equilibrium bounded by the somewhat extended original equatorial drop interface against the water, and by a cylindrical internal surface against the monomer in the centre of the drop. No particles occupy the polar regions of the drop. The loss in volume on polymerization, together with a slight increase in equatorial radius, causes the polar caps of the drop to cave in where the two liquids are in contact.

By contrast, if initiation occurs at the interface, the polymer growing there will transform it into a skin with uniform thickness. Collapse of such structure is most probable in domains of minimum curvature, i.e., along the equator. Interfacial initiation does not occur in isolation. It is always accompanied by homogeneous initiation. The resulting mixed initiation gives rise to hybrid shapes, e.g., the polar caps pushed in undistorted along the latitude defined by the outer edge of the equatorial particle heap.

Sketches of the three basic shrunk shapes are shown in Fig. 4. Figure 5 gives a series of photographs which demonstrate the development of polymerizing drops towards the shrunk shape with mixed initiation.

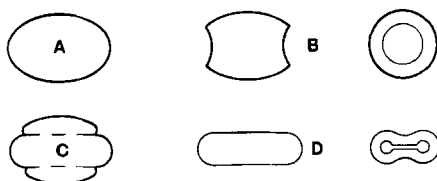


FIG. 4. Schematic drawing of shrunk drop shapes: (A) original; (B) shrunken, homogeneous initiation; (C) shrunken, mixed; (D) shrunken, interfacial initiation.

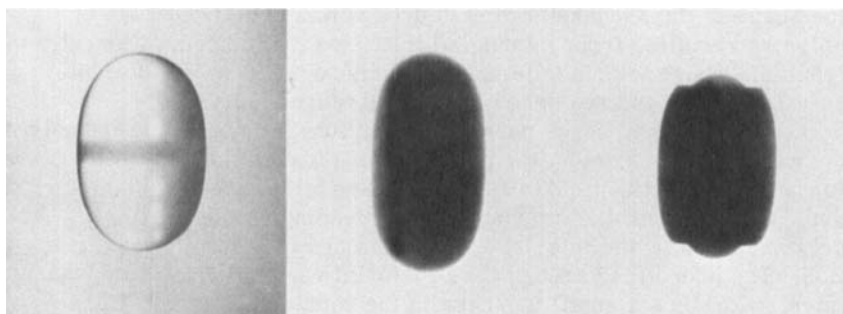


FIG. 5. Photographs of shrinking drops, mixed initiation.

Interfacial initiation occurs when the initiator originally present in the monomer drop is adsorbed by stabilizing agents at the interface. It does not prevent homogeneous nucleation from occurring at the same time.

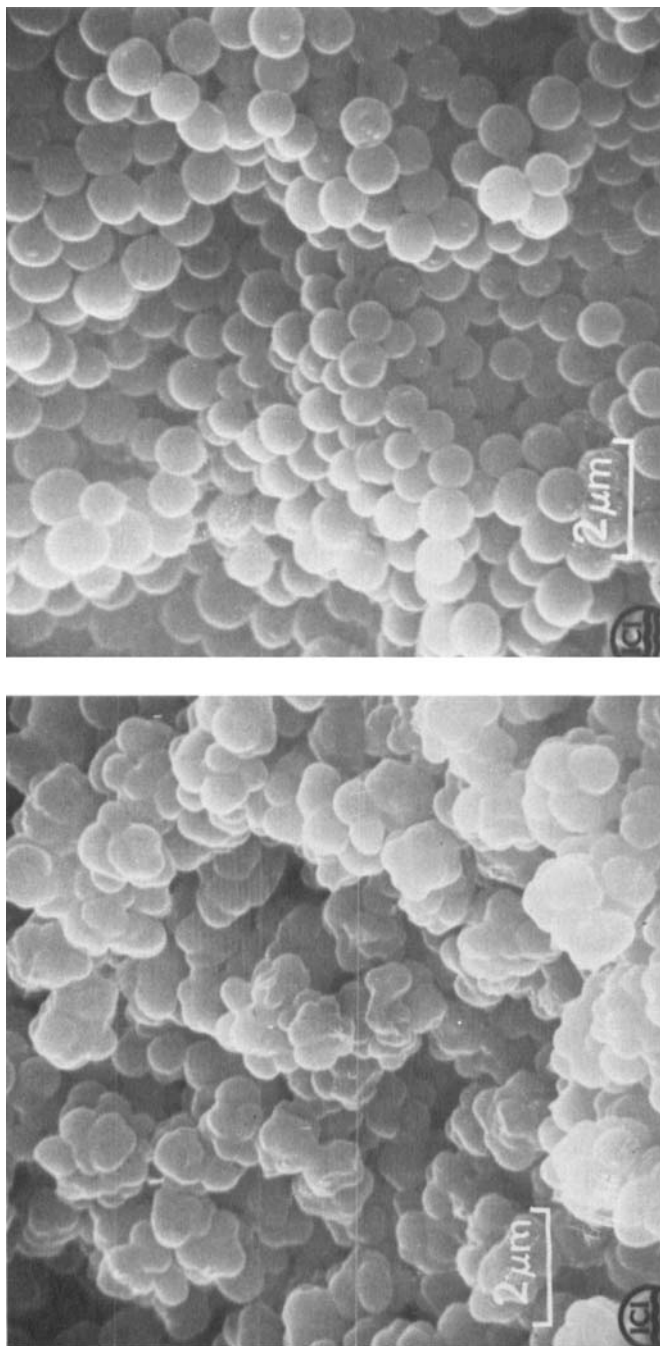
Internal Morphology

The shapes and structures of polymer inside the drop turned granule are made visible by scanning electron microscopy. Two structures are shown in Fig. 6. Both illustrations depict nascent polymer at $\sim 28\%$ conversion. Polymer A was made with 0.2% peroxydicarbonate initiator in the monomer and no further additives. The same initiation was used for polymer B, but here the monomer contained a small addition of an experimental stabilizer. The important difference in morphology between the two polymers is that while polymer B consists of individual spherical particles having roughly the same size ($0.8 \mu\text{m}$), in polymer A compound particles are seen, which appear to be the result of continued polymer growth onto agglomerates of spherical particles. (Note: loss of monomer causes a linear shrinkage of $\sim 15\%$; the particles seen on the photographs are that much smaller than the nascent polymer particles inside the drop).

DISCUSSION

The observation that nascent polymer appears in the form of spherical particles in various stages of aggregation suggests that polymer and monomer constitute a colloid system. Morphogenesis depends in such systems on the relative importance of the rates of nucleation and growth of polymer particles, their Brownian movement and mutual attraction and repulsion. We expect that during the earliest stages of polymerization, soluble oligomeric free radicals exist in solution [4-6]. These grow to some critical size, above which they precipitate to form primary particles. If oligomeric radicals are formed after the first particle nucleation, they have two possible fates: growth to the critical size followed by precipitation or capture by already existing particles.

The number of particles at this stage depends on the rate of initiation. As particle formation continues, the probability of capture increases until finally all oligomers arising in the liquid monomer are captured. Alternatively, particle growth can proceed also if initiation is transferred to monomer swollen particles. If some repulsive force



(A)

(B)

FIG. 6. Scanning electron micrograph, internal polymer morphology: (A) no additive, aggregates; (B) experimental stabilizer, spheres.

prevents the particles which have grown to a certain size from colliding and coagulating, their number should remain constant from now on. In the absence of such force, because the energy gained by satisfying van der Waals attraction far outweighs the kinetic energy of the particles, every Brownian collision between two particles is irreversible, in that it produces one particle with the combined volume of the collision partners. The rate at which the average particle volume increases in such conditions depends linearly on the phase volume ratio of particles to suspending medium and inversely on the viscosity of the latter as shown by Smoluchowsky [7].

In a dilute system, where polymerization, precipitation, and coagulation are in a steady state, one can set the rate of coagulation equal to the rate of polymerization:

$$n(d\bar{v}/dt) = R_{pol} = (4 kT/3 \eta) \phi n$$

where n is the number of particles (m^{-3}), ϕ is the phase ratio, η is the viscosity of the liquid phase, k is Boltzmann's constant, T is the absolute temperature, and $\bar{v} = \phi/n$ is the mean particle volume. Integration and rearrangement gives

$$\bar{v} = (4kT/3\eta) t \int^t R_{pol} dt$$

or more simply, if R_{pol} is assumed constant over a small increment of time

$$\bar{v} = (4 kT/3 \eta) t^2 R_{pol}$$

and

$$1/n = (4 kT/3 \eta) t$$

With $R_{pol} = 1.5 \times 10^{-5} m^3/sec$, an average particle radius of $1.1 \times 10^{-6} m$ is expected after the first 100 sec of polymerization, growing to $5 \times 10^{-6} m$ at ~2% conversion or 1000 sec. However, because observed particle radii at these conversions are around $10^{-7} m$ or less, there must be some stabilizing mechanism at work to account for the apparent lack of coagulation.

One is compelled to conclude that some repulsive force does exist between the particles and significantly reduces the number of effective

collisions. Nothing can be said yet about the nature of this force or the mechanisms of its action; note however that a potential barrier of ~ 15 kT is expected to reduce the frequency of Brownian collisions by a factor of 10^5 and thereby assure colloid stability [8].

Any chemical agent capable of preventing particle collisions will have to act on the surface of the particles, whether it is surface bound or homogeneously present throughout the bulk of the particles. It is likely to be more efficient at higher surface concentrations. If only a limited amount of this agent is present in the monomer phase, its efficiency will decrease as the total surface area of the particles increases. As all particles are expected to grow at the same rate, the efficiency of the stabilizing agent in preventing Brownian collisions will decrease uniformly for all particles. The growth will reach a stage when interparticle collisions begin to occur and doublets begin to appear. Redistribution of the stabilizing agent associated with two primary particles over the total mass or the effective surface of the doublet leads to a stabilizer concentration which is sufficient to prevent doublet-doublet collisions, even if it does not exclude doublet-singlet collisions. The population of doublets and triplets resulting from this agglomeration process will continue growing in size as polymerization carries on, until a new threshold of instability is reached and further agglomeration sets in. Figure 7 gives a schematic illustration of the sequence of events.

However, this idealized mechanism can be valid only for strictly monodisperse particle populations. In real systems where the particle size distribution has a finite width, the individual aggregation steps will run into each other. If the number of contacts between particles is a measure of the stability of particle clusters or

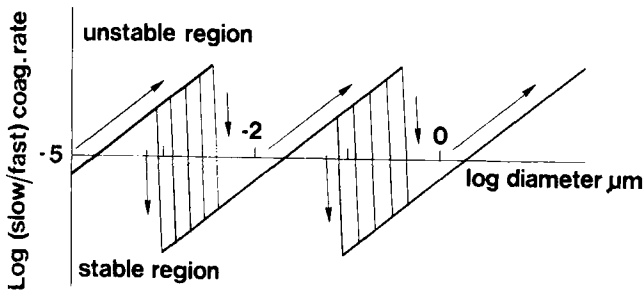


FIG. 7. Schematic representation of particle growth and colloid stability.

aggregates, then the 13-particle randomly close-packed aggregate comprising a central particle surrounded by 12 touching neighbors represents a more stable configuration than any smaller cluster: each of its peripheral particles is in contact with five neighbors. One would expect to find this aggregate as a building block in larger structures as seen in Fig. 6A.

The shapes of the primary particle aggregates depend also on the deformation suffered by the original spheres on aggregation and on the mode of subsequent growth. The collision of purely viscous (liquid) spheres would lead to coalescence, when two equal spheres of radius 1 produce after collisions a single sphere with radius $2^{1/3}$.

With elastic particles, collisions lead to slightly distorted doublets: the deformation depends on the work expended in achieving it and the amount of van der Waals and interfacial energy gained in the process. In equilibrium these two must balance [9].

If the aggregated polymer particles remain essentially spherical and keep on growing in a direction perpendicular to any polymer-monomer interface, one can deduce the shapes aggregates will show at various times after aggregation. This is demonstrated in Fig. 8. The size of the primary particles at the time of aggregation can be estimated from the distance between the centers of neighboring spheres in an aggregate. If, in addition, one has an estimate of the average size of the aggregates, one can deduce the conversion at which the last aggregation step has taken place.

The growth ratio of an aggregate from the time of aggregation to the time at which the reaction was stopped can be defined as

$$R_g = (V_A - nV_p) / nV_p$$

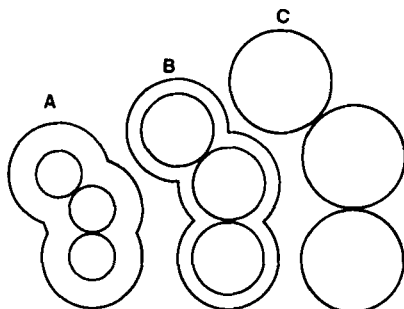


FIG. 8. Schematic drawing of aggregate shapes: (A) old; (B) medium; (C) fresh.

where V_A is the final volume of the aggregate, n is the number of primary particles in the aggregate, and V_p is the volume of the primary particles at aggregation. Let us take the aggregates seen in Fig. 6A to be the 13-particle clusters discussed above and assume that the radial growth on the primary particles since aggregation is equal to the original particle radius. The radius of the original aggregate (at formation) taken as a solid sphere, assuming a void volume fraction of 30% between the primary particles, is then:

$$r_{A0} = (1.3 \times 13)^{1/3} r_0 = 2.57r_0$$

where r_0 is the radius of the primary particle at aggregation. The final aggregate volume is now estimated by

$$V_A = (4/3)\pi (2.57r_0 + \Delta r)^3$$

where $\Delta r (= r_0)$ is the radial growth on the primary particle.

With these parameters, the growth ratio is estimated as

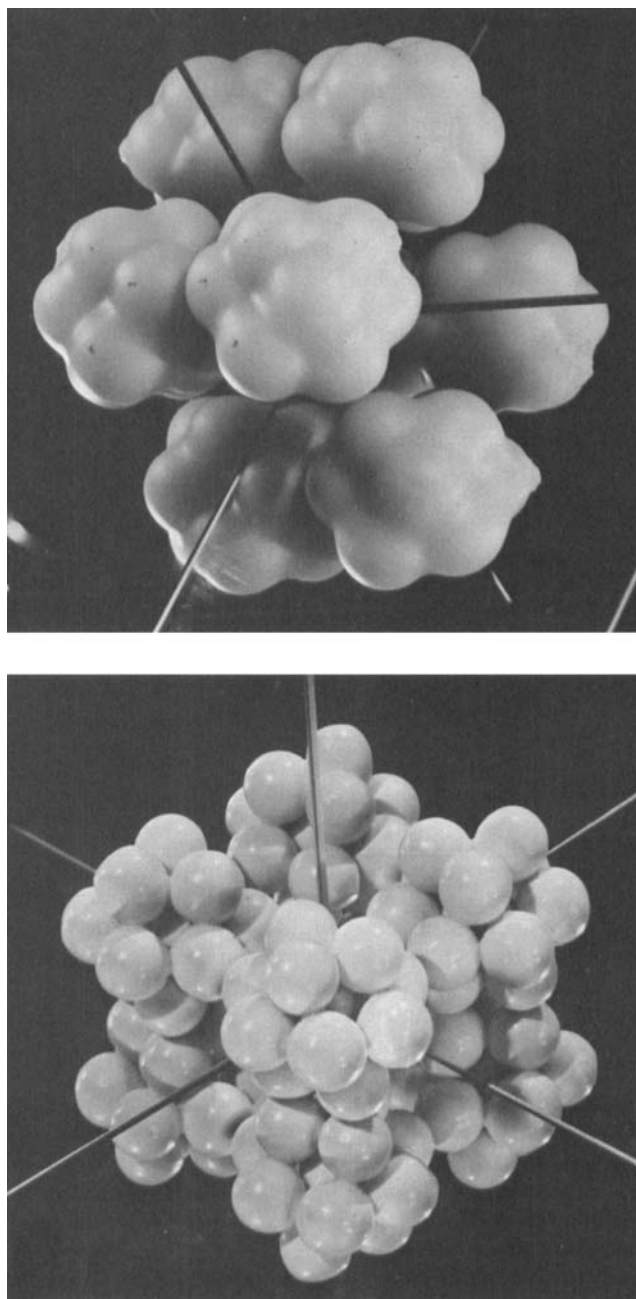
$$R_g = [(2.57 + 1)^3 - 13]/13 = 2.47$$

This indicates that the final aggregation into the clusters containing an estimated 13 primary particles took place at a conversion of $28/2.47 \approx 11.4\%$.

Models of a freshly formed 13-particle cluster and of the effect growth has on this shape are shown in Fig. 9; the resemblance to the SEM pictures of Fig. 6 is evident.

Aggregate size and the amount of polymer growth after the last aggregation step or the conversion at which this step occurs, are clearly the major factors influencing the eventual morphology of the fully polymerized material and hence its porosity.

The inertial suspension of a polymerizing drop of monomer simulates and idealizes the situation of a polymerizing monomer drop in industrial dispersion polymerization. The spinning drop does not contact any solid surface, it is subject to a controllable, well defined force field, and does not undergo random deformations and accelerations; changes in its shape and volume can be monitored. These features make this technique eminently suitable for the study of the complex colloidal phenomena of precipitation polymerization.



(A)
FIG. 9. Photographs of 13-particle aggregate model: (A) at aggregation; (B) after growth.
(B)

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The enthusiastic cooperation of Arthur Cobbold, Karen Higgins, Frank Willmouth, and John Wilson is gratefully acknowledged.

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DISCUSSION

Dr. S. Porrvik (Kema Nord AB, Sundsvall, Sweden): Dr. Zichy showed some very interesting scanning photographs in which the primary particles were almost all separated from each other. My question in this connection may be divided into three parts. First, has it been possible to keep these individual primary particles up to the commercial conversion—that is, about 80%? I understand Dr. Zichy's conversion was about 20%.

If he has been able to keep the primary particles isolated up to that point what influence do these particles have on properties during processing—for example, the speed of fusion and rheological properties? We might perhaps expect such a polymer to behave in a similar way to an emulsion type of polymer.

Thirdly, if it is possible to keep these particles up to the 80 or 90% conversion, is it still possible to use the low amount of additives usually present in suspension polymers? If it is a pure suspension

polymer, I would guess that to maintain these particles as individual particles up to this level of conversion about 1% of additives would have to be added.

Dr. Zichy (I. C. L., Welwyn Garden City, U. K.): In reply to the first question, we did not go on to higher conversions because the drop becomes unstable and is no longer supported in the center of the axis of rotation. We do not know what happens at higher conversions. That also answers the third question.

In answer to the second question, with respect to the rheological properties of PVC, I do not think that it is these large particles which are of such importance as the smaller ones about which Dr. Geil talked, and which are perhaps vestiges of crystallinity or have some other unknown cause for their existence.

There must be something which acts like a filler in ABS in order to give us the rheological properties which are found in PVC, but there is no indication that the large particles are the culprits.

Dr. J. B. Pompon (Rhône Poulenc Polymères, Saint Alban, France): On a similar subject, Dr. Zichy has talked about a colloid which was partially soluble in a monomer and partially at the interface. What special characteristics has he found for the final PVC with this type of colloid?

Dr. Zichy: Could Dr. Pompon clarify what he means by "colloid" please?

Dr. Pompon: A suspension in PVA or something similar.

Dr. Zichy: We have made these extremely small particles of PVC which, in one reaction run, might amount to perhaps 50 mg of PVC. This may not be the right sample on which to do rheological studies. I cannot answer the question.

NOTE ADDED IN PROOF

The author became aware of the analogy between cluster formation from primary PVC particles and clustering on the atomic scale after the completion of the manuscript. [See, M. R. Hoare and P. Pal, J. Cryst. Growth, 17, 77 (1972)].