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# Structure of High-Internal-Phase-Ratio Emulsions

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## INTRODUCTION

The structure of high-internal-phase-ratio emulsions was treated, theoretically and mathematically, in a paper presented at the National Colloid Symposium in 1966 (1). At that time, certain postulates were proposed to explain the rheological properties of these emulsions on the basis of the geometry of the particle packing. Certain predictions were made concerning behavior in the 94–96% internal phase region. These predictions have since been confirmed by independent investigators (2). Attempts were made at several laboratories to obtain photographs of the emulsion structure using conventional light microscopy and phase-contrast microscopy. None of these attempts were particularly successful, since the structure was distorted by the slide making process.

Since then, it has become possible to “freeze” the structure of these emulsions by polymerizing one of the phases and taking scanning electron photomicrographs. In the first series of studies made using this technique (3), a high-internal-phase-ratio emulsion of water in resin was made and the resin external phase was polymerized. The block of polymer was then broken and SEM pictures made of the internal structure.

In this series of studies, we are using a polymerizable internal phase, vinyl chloride,

and making oil in water emulsions. The effects of phase ratio, catalyst ratio, and preparation method were studied. In addition to the SEM photographs, the molecular weight distribution of the polymers was determined by gel permeation chromatography and intrinsic viscosity measurements.

## EXPERIMENTAL

*Emulsion polymerization.* All polymerizations were carried out in the glass reactor system shown schematically in Fig. 1. The external phase of the emulsion was prepared by mixing equal parts by weight of water and Emulsifier EXP-1 (a proprietary emulsifier blend supplied by Petrolite Corporation). Di-(2-phenoxyethyl)-peroxydicarbonate was the low-temperature free-radical initiator used (supplied by Lucidol Division of Pennwalt Corp.). The reaction vessel was charged with water, emulsifying agent, and initiator. The reactor cap and valving assembly were attached, and the reactor sealed. After weighing, the reactor was connected to an inverted vinyl chloride cylinder at union (C). Liquid vinyl chloride was fed in through the flexible Teflon tubing in 3–5 ml increments at a temperature of less than 25°C by opening valve (B). It was necessary to vent the reactor at valve (A) periodically in order to equalize pressures between the

reactor and the cylinder. After each addition of vinyl chloride, all valves were closed and the reactor shaken by hand in a manner designed to give maximum possible shear. In order to prevent breaking the emulsion, it was necessary to emulsify thoroughly each incremental amount of vinyl chloride before additional monomer was added. This was particularly critical at high monomer:water ratios. Total emulsion preparation time was about 20 min. The amount of monomer added to the system was determined by disconnecting union (C) and again weighing the container and valving assembly. When the desired amount of vinyl chloride had been introduced, the reaction vessel was detached from the cylinder at union (C) and immersed in a constant temperature bath at 36.0°C. At this point, no detectable polymerization had occurred. The emulsion was allowed to polymerize for 48 hr or until the reactor contents were solid.

*Scanning electron microscopy.* The vacuum-dried bulk polymers were fractured and samples were mounted on copper discs prior to gold vacuum metallization. The metallized samples were examined utilizing a JEOLCO JSM-2 scanning electron microscope.

*Characterization of the Polymers.* In order to characterize the polymers, intrinsic viscosity determinations and gel permeation chromatography in tetrahydrofuran were performed. The viscosity measurements were made using a No. 5 Cannon-Ubbelohde viscometer at 30°C, and a Waters ANA-PREP chromatograph was utilized to obtain molecular weight distribution data. Before measurements were made, the emulsified polymers were vacuum dried at 50–60°C and dissolved in tetrahydrofuran. The polymers were then precipitated in methanol, filtered, washed with methanol, dissolved in tetrahydrofuran, and freeze dried. This procedure removed surfactant from the polymers which would interfere with the dilute solution measurements.

## RESULTS AND DISCUSSION

The ease of formation of the emulsions was dependent upon several parameters. The

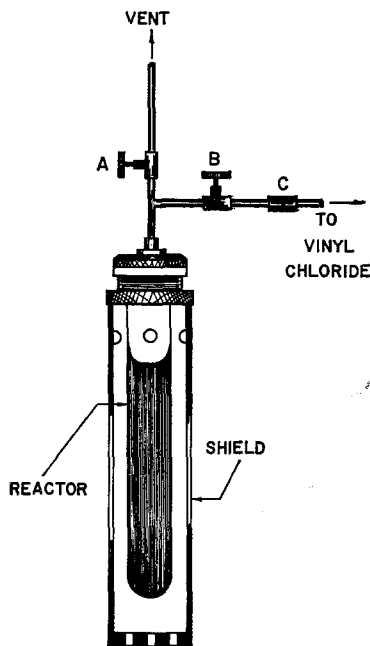


FIG. 1. Schematic of reactor and valving assembly.

amount of monomer added incrementally was critical. The addition of too much vinyl chloride caused the existing emulsion to break and to separate into two phases. Once phase separation had occurred, it was extremely difficult or impossible to reestablish the emulsion. The low water phase emulsions were very sensitive to the amount of initiator present. It was impossible to form 90:10 and 95:5 emulsions at high initiator concentrations. The initiator apparently affects the relative solubility of the emulsifier in the two phases.

The high ratio emulsions, when polymerized, formed rigid, friable polymer after about 8 hr reaction time. These polymers were chalky in appearance. The 70:30 and 50:50 emulsions were also chalky in appearance, but were more friable than the 90:10 and the 95:5. The 20:80 emulsions formed suspensions of polymer in the fluid external phase. The rate of polymerizations was slower at low ratios than at high ratios of monomer:emulsifier. Polymerizations carried out in emulsions containing 70% or more vinyl chloride were essentially quantitative.

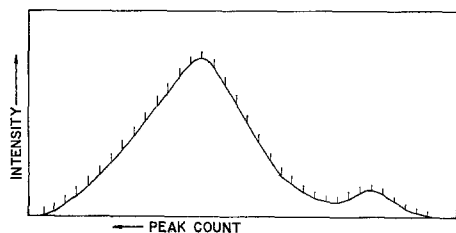


FIG. 2. GPC trace of polyvinyl chloride from a 95:5 emulsion.

Di-(2-phenoxyethyl)-peroxydicarbonate was chosen as the initiator because of its low half-life temperature. When more common initiators, such as benzoyl peroxide or AIBN were employed, temperatures necessary for polymerization caused breaking of the emulsion.

Figure 2 shows a GPC trace of 95:5 (monomer:water) ratio polymer with a catalyst:monomer ratio of 6.66 mg/g. A major and a minor peak are evident and were typical of the chromatograms obtained. The minor peak of the bimodal distribution was more pronounced as the monomer:water ratio was increased; approximately 3% at 50:50 and increasing to 7% at 95:5. The peak molecular weight of the minor peak was always in the range of  $1 \times 10^6$  to  $2 \times 10^6$ . The peak molecular weight of the major peak varied with the monomer:water ratio at a constant catalyst concentration as shown in Table I. The molecular weight distribution ( $M_w/M_n$ ) of the major peak was always in the range of 2.6–3.0. It was also found that the peak molecular weight decreased as the catalyst:monomer ratio increased for a constant monomer:water ratio. Preliminary evidence indicates that the minor high molecular weight peak is formed

TABLE I

Monomer:Water Ratio	Peak Molecular Weight (Major Peak)
20:80	90,000
50:50	168,000
70:30	172,000
90:10	218,000
95:5	230,000

TABLE II

Monomer:Water Ratio	$[\eta]$ , dl/g	$k'$	$k' + k''$
20:80	0.98	0.43	0.54
50:50	1.23	0.42	0.53
70:30	1.40	0.40	0.52
90:10	1.44	0.44	0.54
95:5	1.60	0.40	0.50

after the polymer has initially gelled and that the magnitude of the high molecular weight portion is a function of the catalyst:water ratio (catalyst/monomer  $\times$  monomer/water) and the time the polymerization is allowed to continue past the gel point.

Intrinsic viscosity  $[\eta]$  measurements were made on the series of polymers reported in Table I. These data are reported only as  $[\eta]$ . Because of the bimodal distributions, any attempt to calculate a viscosity average molecular weight by the Mark-Houwink-Sakurada relationship would not be completely meaningful. Table II shows the intrinsic viscosity and the Huggins constant as calculated from the Huggins and Kraemer equations.

The values for  $k'$  reported here appear high for the molecular weight ranges under consideration. Recent evidence indicates that dissolution may not be complete using routine procedures and that long time periods are required to obtain acceptable scattering values at low angles less than  $45^\circ$  (4).

To minimize this effect, all polymer solutions were allowed to equilibrate for 48 hr before viscosity determinations were made. Utracki reported a more extensive tabulation of interaction constants for polyvinyl chloride prepared by ultraviolet irradiation, bulk, suspension, and emulsion techniques (5).

Figure 3 and Table II show how  $[\eta]$  changes as a function of the monomer:water ratio at a constant catalyst:monomer ratio of 6.66 mg/g. Figure 4 shows the change in  $[\eta]$  as a function of a catalyst:monomer ratio at a constant monomer:water ratio of 70:30. These results are typical of those obtained under other conditions. It is of interest to note that

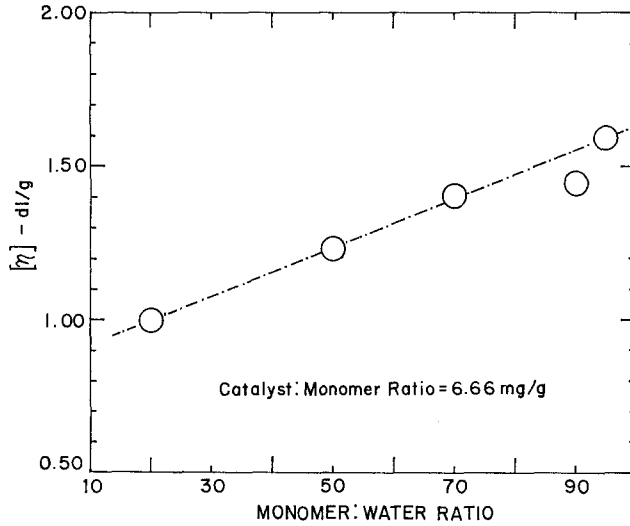


FIG. 3. Intrinsic viscosity as a function of the monomer:water ratio at a catalyst:monomer ratio of 6.66 mg/g.

polymers having the same  $[\eta]$  can be produced under different conditions; e.g., polymers having an  $[\eta]$  of 1.58–1.60 can be produced using a monomer:water ratio of 95:5 and a catalyst:monomer ratio of 6.66 mg/g or a monomer:water ratio of 70:30 and a catalyst:monomer ratio of 3.33 mg/g.

To summarize briefly, the molecular weight of the major peak increases with a decrease in the amount of catalyst and increases with an increase in the internal ratio. The intensity of the secondary peak increases with an increase in phase ratio.

The SEM pictures show that the situation is in many ways similar to that encountered in the previously studied water in oil emulsions (3). Since emulsions are “constructs,” their

structure and behavior often depend as much on the method of preparation as on the chemical constituents involved. In situations where the high-internal-phase-ratio emulsions were

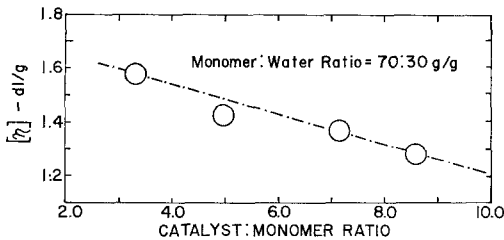


FIG. 4. Intrinsic viscosity as a function of catalyst:monomer ratio in 70:30 emulsions.

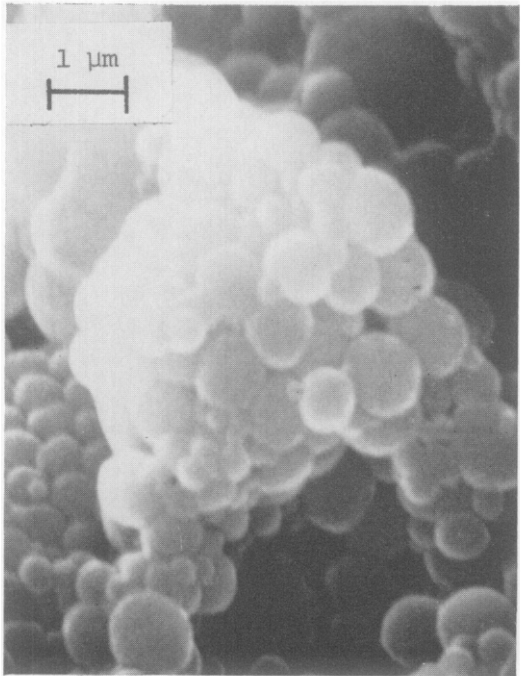


FIG. 5. Polyvinyl chloride from 90:10 emulsion at 10,000 $\times$ .

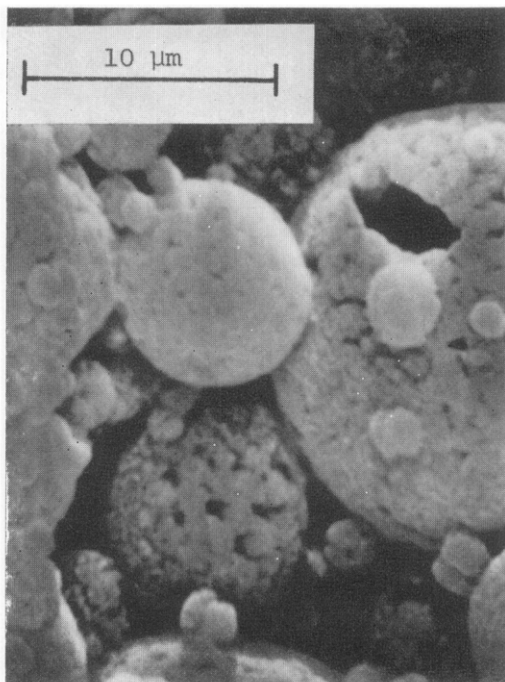


FIG. 6. Polyvinyl chloride from 50:50 emulsion at 3000 $\times$ .

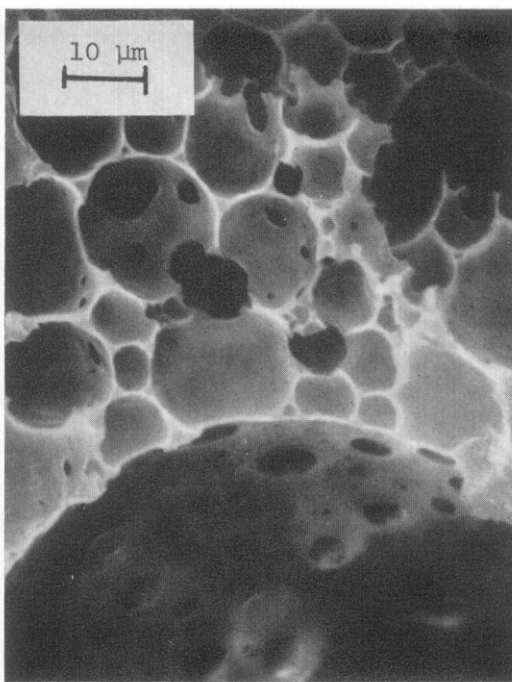


FIG. 8. Polystyrene from a water in oil emulsion at 1000 $\times$ .

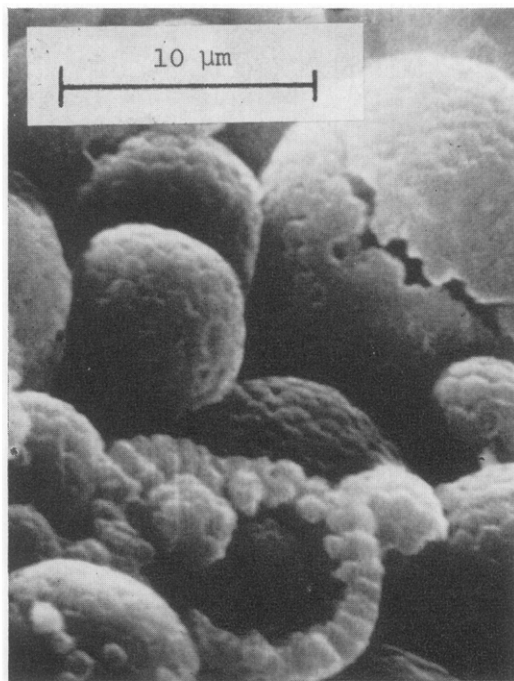


FIG. 7. Polyvinyl chloride from 90:10 emulsion at 3000 $\times$ .

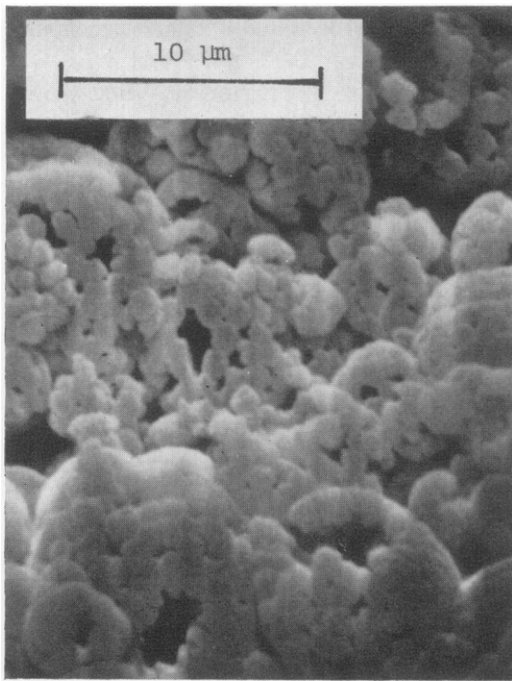


FIG. 9. Polyvinyl chloride from 95:5 emulsion at 3000 $\times$ .

subjected to sufficient shear to assure optimum mixing, it was found that the droplets were relatively monodisperse and that their packing configurations were in close agreement with the predicted geometric models.

Figure 5 illustrates this nicely. This is a 10,000 $\times$  picture of an emulsion which contained 90 volumes of vinyl chloride in 10 volumes of aqueous phase. However, in situations where the rheology of the emulsion prevented adequate mixing in the later stages, relatively polydisperse configurations were obtained. Figure 6 shows the polymer obtained from an emulsion containing 50% internal phase. Note that it is highly polydisperse, and that there is a good deal of space in between the droplets. Figure 7 shows the polymer obtained from a 90% internal phase emulsion. This emulsion also was quite viscous and difficult to mix. It is again polydisperse and the droplets are much more closely packed. Figure

8 is a micrograph of one of the previously reported water in oil emulsions. Here we have polymerized the external phase and the internal droplets are represented as "holes." Figure 7 shows the situation where the internal phase was polymerized and solid droplets are present. Both emulsions were polydisperse and the spherical droplets which appear in Fig. 7 would almost fit into the "holes" shown in Fig. 8. Figure 9 shows the polymer obtained from a 95% internal phase vinyl chloride emulsion. Here the crowding is extreme and the droplets are much more monodisperse.

Recent work on the random packing of spheres and circles (6, 7) has shown that the ideal packing ratio of 74+ % is never attained because, apparently, unfillable holes occur at random in the emulsion matrix.

The criteria for the occurrence of a stable "hole" in the closely packed matrix are that each droplet, or sphere, on the periphery of the

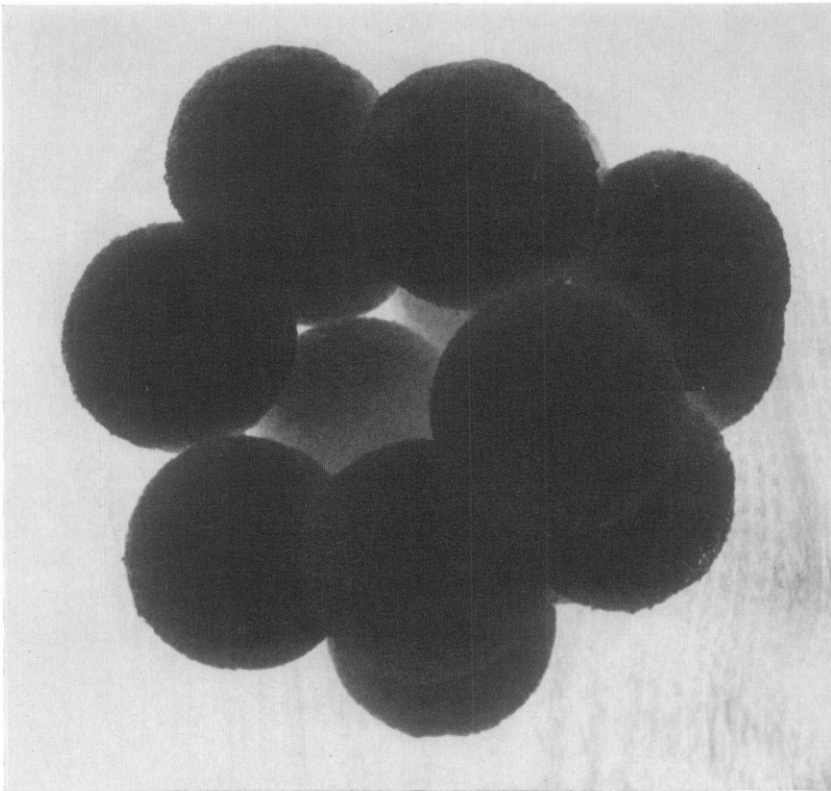


FIG. 10. Singlet "hole" in spherical packing.

hole must contact at least four other spheres and the points of contact must not all be in the same hemisphere nor lie on a single great circle.

Figure 10 shows one type of hole produced by the omission of a single droplet. Figure 11 shows a somewhat larger hole whose peripheral droplets lie at the vertices of a tetrakaidecahedron. Figure 12 shows another picture of a 95:5 emulsion. Some of the configurations in this picture bear a marked resemblance to Figs. 10 and 11. Note also in Fig. 9 similar configurations.

Figures 6 and 7 contain what seem to be hollow spheres made up of closely packed polymeric particles. In Fig. 6 a portion of the shell of one of the spheres has broken out, and in Fig. 7 one of the spheres is cracked and another one broken approximately in half. The

question arose as to whether the original emulsion particles are represented by the large spheres or by the small pieces which seem to make up the shell of the sphere. Figures 6 and 7 are shown at a magnification in the neighborhood of 3000 $\times$ , and, therefore, the large hollow particles range in size from about 1 to 10  $\mu\text{m}$ . This is the size range obtained in other studies, and, therefore, we believe that the large spheres represent the original emulsion droplets. How can hollow spheres be explained? A simple calculation offers a possible explanation. The density of monomeric vinyl chloride is approximately 0.92. The density of polyvinyl chloride ranges from about 1.2 to at least 1.4. This means that 100 ml of monomeric vinyl chloride would weigh approximately 92 g, and when this amount of vinyl chloride was allowed to polymerize it would occupy about 73–77 ml.

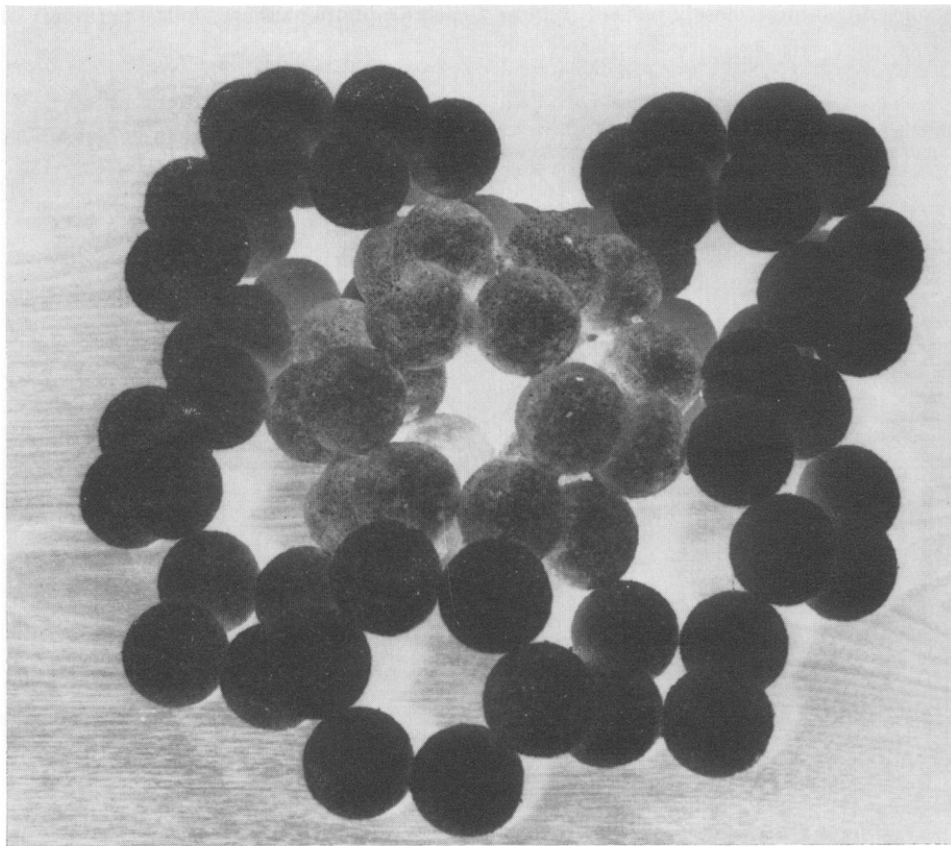


FIG. 11. Stable "loose" packing.



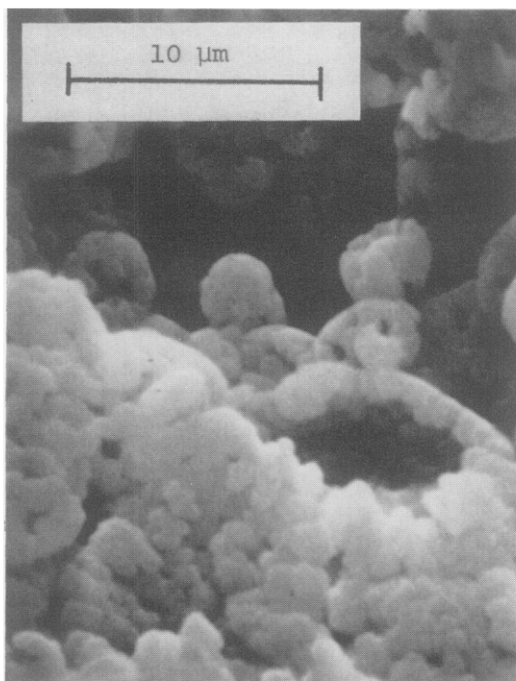


FIG. 12. Polyvinyl chloride from a 95:5 emulsion at 3000 $\times$ .

Assuming that polymerization is initiated on the surface of the spherical droplet at a number of sites and that as the polymers grow from these sites they distribute themselves optimally on the surface of the sphere and grow until they fill the entire surface of the sphere, a rigid shell of polymer with unreacted monomer inside would result. Polymerization would then continue until all of the monomer was utilized. However, additional initiator would be unable to penetrate the rigid shell. Assuming on the basis of our previous calculations, that the shell would constitute approximately 75% of the volume of the original sphere, we would find that this shell would be from 30 to 40% of the radius in thickness. The broken hemisphere in Fig. 7 shows a thickness in this general range.

This mechanism would also explain the high molecular weight secondary peak in the poly-

mer molecular weight distribution, since the last portion of monomer would add to the already formed sites and not have access to any additional initiator. Further, it would explain why the molecular weight is higher for the emulsion with higher phase ratio and why the secondary peak is more prominent in these emulsions, since here the closer crowding and greater number of droplets would tend to stabilize the shell of polymer more quickly than in the less crowded emulsions.

### CONCLUSIONS

1. Although the actual conditions encountered in preparing the emulsions and conducting the polymerizations are much more complex than postulated in the simple geometric theory, the structures actually found by SEM techniques seem to approach the ideal structures quite closely.

2. Even in the case of polydisperse systems, the structures of the water in oil and oil in water emulsions are sufficiently alike to show that geometry is playing a dominant role.

3. The fine structure of the individual polymerized vinyl chloride droplets is unexpectedly complex. Any explanation of this phenomenon must take into account the bimodal molecular weight distribution and the way it varies with the monomer-to-water ratio and the catalyst-to-monomer ratio.

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