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Structural studies of organic gels by SEM

Z. BLANK, A. C. REIMSCHUESSEL
Materials Research Center, Allied Chemical Corporation, New Jersey, USA

Results of an examination of vacuum freeze-dried organic gels by scanning electron microscopy (SEM) are presented and discussed in relation to the potential use of such gels as crystal growth media. The organic gels which were studied included polyacrylamide, polyethylene oxide and polyvinyl alcohol – all prepared by radiation cross-linking in aqueous solutions.

It was concluded that both polyacrylamide and polyethylene oxide gels appear to be suitable as growth media from a structural point of view whereas polyvinyl alcohol gels do not look promising. Some growth experiments confirm these conclusions.

1. Introduction

While the growth of single crystals in gels has only been relatively recently proposed as a technique for the preparation of certain materials of interest in solid state electronics [1], the process has been known for a long time. As a matter of fact, gel growth had been proposed as accounting for the natural growth of many crystalline minerals [2]. It has been theorized that in gelatinous media, under suitable environmental conditions, reactions can occur which result in the formation of crystalline veins. Accordingly, natural quartz was at one time a gelatinous silicic acid and a combination of time and temperature caused slow dehydration to take place yielding eventually hard silica rock [3].

The effects of gelatin gels on the nucleation and growth of silver halide crystals in photographic emulsions have been studied extensively [4, 5]. The researchers believe that the gelatin plays an important role in the crystallization process. The formation of sugar crystals in fruit jellies [6] and the formation of magnesium ammonium phosphate crystals during putrefaction of meat [7] have been noted as further examples of natural crystal growth in gel media. In a related vein, the mineralization of biological tissues, an aspect of the precipitation of crystals in a colloidal matrix, has been the subject of several articles [8].

Recently, organic gels have gained some recognition as potentially useful growth media. Gelatin gels have been used for the growth of KDP [9], alkaline earth ortho-phosphates [10] and $CaCO_3$ [11]. Sodium zeolite crystals have been grown in Carbopol 934® Gels (Acrylic acid gels, B.F. Goodrich Chemical Co, Ohio Product) [12], $CaCO_3$ in polethylene oxide gels [11] selenium in styrene–maleic anhydride gels [13], and HgS in polyacrylamide [gels 26].

2. Theory of gel structures

The following section attempts to present a general qualitative description of what might be considered a unifying theory of gel structures as related to their application as crystal growth media. No attempt is made to derive any quantitative relations describing kinetic factors involved in gel formation. The purpose of this section is to enable scientists in the field of crystal growth in gels to better design their systems and explain their experimental observations.

While it was recognized long ago that the characteristics of gel systems can be best explained on the basis of a two-phase system there have been controversies about the exact model. Some unique properties of gel systems are related to the nature of the solid phase while others stem from the nature of the liquid phase.

2.1. The liquid phase

Gels can be considered as two-phase liquid–solid systems whose unique properties can be partially attributed to the fact that the liquid can exist in three states [14], namely:

(1) free liquid contained in larger cavities;

(2) liquid retained in the capillary pores between micellae;

(3) liquid absorbed in thin skins at the surface of the micellae.

This early model [14] is compatible with more recent ones proposed by Aizawa and Suzuki [15] and Drost-Hansen [16] which are generally described as the "three layer model". According to Drost-Hansen [16] vicinal water (close to a solid surface, or first layer), which is structured differently from that of bulk water, may extend over considerable distances from the surface. For example, the ordered structure can extend from tens to thousands of molecular diameters, i.e. from 2×10^{-3} μm up to 0.5 μm. An intermediate or second "state" of disordered water may exist, at least in some cases, between vicinal water and the disordered bulk, or third layer.

Based on the "three-layer model" of the liquid phase in the vicinity of solid surfaces it appears that at least in some gels, a great portion of primary channels would appear to contain liquid of mostly layered structure extending across the entire pore diameter. Obviously, under such conditions the nucleation behaviour cannot be explained simply on the basis of a heterogeneous mechanism. Moreover, it is quite possible that the liquid phase in silica gels resembles "polywater" in many respects [16], and as such can be expected to have an appreciable effect on the thermodynamics of the nucleation process. Also, the effect of concentration of electrolyte in the liquid phase has to be taken into account in so far as its relation to the solubility of the crystal forming compound. Cope [27] used NMR spectram of sodium ions to study the solubility of sodium in the interstitial water of actomyosin gel. It was found that solubility in this (gelled) water was considerably lower than the solubility in bulk water, suggesting that the water in the gel is structured into an "ice-like" state as a result of the actomyosin molecule/water interface interactions. This would explain why nucleation in gels appears to occur at relatively low supersaturations.

One additional factor to consider is the effect of a structured liquid layer on the diffusion of ions. Gast [28] observed decreased diffusion of sulphate ion in clay suspensions compared to ordinary water solutions. His interpretation is that a decrease in energy of activation for diffusion is observed because of the introduction of an intermediate disordered layer between the liquid bulk phase and the more ordered bound water adjacent to the solid surface. Hence, it seems that reduced diffusion rates should counteract the effect of increased supersaturation in gels in so far as their mutual effect on nucleation is concerned.

2.2. The solid phase

2.2.1. *The cellular structure theory (micellar theory)*

The micellar theory views the gel as consisting of small liquid droplets held up in a solid cellular structure. The formation of a cellular structure can be initiated when the gelation process precipitates material along the solid-liquid interface [17]. This process occurs when the growth-rate of the solid phase is faster than the homogeneous nucleation in the liquid phase. The "crystallization" of the solid phase cannot proceed through the whole mass by a homogeneous nucleation mechanism, and the formation of cell walls at the solid-liquid interface is induced [18].

Many gels such as gelatin and agar which are prepared by physical means (i.e. cooling of hot solutions), rather than chemically, are known to exhibit cellular structure. These gels could be termed "physical gels" in contrast to "chemical gels". It is a characteristic of such gels that the supersaturation period (the time period during which the gel solution becomes supersaturated) tends to be short, typically a few minutes.

A cellular structure in gelatin gels has been proposed on the basis of microscopic studies showing minute solid cells joined in a somewhat irregular manner [18]. More recent evidence of cellular structure of such gels was reported by Halberstadt *et al.* [19], based on SEM photographs of freeze-dried specimens. The structure of gelatin gels has been associated with its preparative technique, more specifically the cooling rate. Faster cooling rates reportedly [20] bring about formation of structures with smaller "cells". Halberstadt *et al.* [19] also noted some cellular structures in basic silica gels. They were described as loosely bound platelets which appear to lack cross-linkages. This observation supports the view suggested earlier that fast gelation rates, as occur in the formation of basic silica gels, lead to cellular structures. A phenomenological explanation for the formation of cellular structures, based on molecular dynamics considerations, has been given by Arsem [21] who concluded that gel formation is quite favourable in cases of dissolved polymers with asymmetrical molecular units and bulky side-groups (for example, gelatin).

2.2.2. The fibrillar structure theory

This theory best describes the nature of chemical gels. It postulates a solid and a liquid phase, both continuous, with the solid forming a fibrous structure and containing the liquid in the pores. Such gels lack thixotropy and they exhibit so firm a structure that bond rupture is difficult even when subjected to ultrasonic waves. When subjected to a disturbance after gelation they will not self heal or reweld together*.

The fibrous type structure should possess a large degree of elasticity as do silicic acid gels and radiation (or chemical) cross-linked organic gels. Mechanical distortion should cause a change in shape of the filaments with an increasing resistance to further distortion. Apparently this involves a straightening out of irregular chains rather than a stretching of each filament. When these are extended beyond a certain point, the structure breaks as a result of the chains' high modulus of elasticity.

In a typical structure two kinds of capillary channels are observed, i.e. coarse "secondary" channels which obey capillary theory, and "primary" channels of nearly molecular dimensions. An approximate calculation shows that the primary channels can attain a length of 45 μm [3]. They must, therefore, be quite twisted in their course. SEM studies of polysilicic acid gels suggest that the gel skeleton consists of fibrillar structures made up of "threads" [19]. These threads form networks possessing a high degree of regularity and orientation as well-ordered bundles of filamentous formations. They develop as a result of the relative ease with which silicic acid or other monomers such as acrylamide or vinyl alcohol polymerize.

3. Experimental

3.1. Preparation of gels

The following gel systems have been prepared for structural studies:

(a) Cyanogum 41® – American Cyanamide Co, N.Y. – a mixture of 95 wt % acrylamide and 5 wt % *N,N'*-methylenebisacrylamide. This mixture after dissolving in water (2.5 and 4.0 wt %) and filtering was cross-linked by irradiation employing ^{60}Co as the source. Total irradiation dose was 2.5 MR at 0.1 MR h^{-1} dosage rate.

(b) Polyox WSR-301® (polyethylene oxide) – average mol. wt. = 4×10^6, product of Union Carbide Corp, N.Y. The polymer was dissolved in water in accordance with recommended procedures [22]. The resulting 1 wt % solution was filtered under pressure through a "Metricel" filter (Gelman Instrument Co, Michigan, average pore size 5 μm) to ensure removal of extraneous solid particles such as undissolved polymer, dirt and other impurities. It was then cross-linked as described above.

(c) Elvanol 72-60® – (polyvinyl alcohol) viscosity 55 to 60×10^{-2} P of a 4% solution at 20°C, 99.0 to 99.8% hydrolysed, product of Dupont de Nemours, Wilmington, Delaware. A solution was prepared by dissolving 3.5 wt % of the polymer in water, filtering under pressure (as above) and subsequently cross-linking as above to produce a gel.

The solid contents of the gel forming mixtures were determined as the minimum concentration that would yield a gel capable of supporting the top solution and the growing crystals. In all the above gels syneresis was less than 2 vol %.

3.2. Preparation of samples for SEM

To preserve the three-dimensional morphology of the gels, specimens were prepared for observation by freeze-drying, a method which reduces problems such as shrinkage and surface-tension deformation associated with air-drying.

Small cubes of ≤ 1 mm^3 were removed from the samples without any deformation, placed on to electron microscope grids and rapidly transferred into a pre-chilled Denton Vacuum DFD-2 Freeze-Drying Unit. Sublimation of the frozen liquid was accomplished by maintaining a temperature of − 80°C at 10^{-2} Torr for a minimum period of 24 h.

The freeze-drying step was immediately followed by vacuum deposition of a thin (~ 150 Å) Au/Pd film to render the specimens conductive.

The instrument used for this study was a JEOLCO JSM-2 scanning electron microscope operated at an accelerating voltage of 25 kV. Photomicrographs were prepared at a scan speed of 50 sec per frame.

4. Results and discussion

Fig. 1 shows electron micrographs representing typical structures of the organic gels prepared as described in the previous section.

The structure seems to possess a continuous solid phase with the individual pores separated

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*It is for this reason that considerable care must be taken in order to avoid bubble formation during gel preparation, since once formed, they remain stable and do not collapse.

TABLE I Gel structures dimensions

Type of gel	Pore diameter (μm)	Wall thickness (μm)	Method of determination	Reference
Silica gel (pH = 5.5) (2.5 wt %)	5×10^{-3}	—	Diffusion of solution	[25]
(0.4M) dense, (pH ≃ 5.0)	<0.1 to 0.5	greater than in low density gel	SEM	[19]
(0.2M) light, (pH < 5.0)	<0.1 to 4.0		SEM	[19]
Gelatin	1.0 to 40	—	SEM	[19]
Polyacrylamide (Cyanogum 41®) (25 wt %)	2 to 10	0.3 to 1.0; extensions ~ 0.1	SEM	Present work
(4.0 wt %)	2 to 15	Up to 200 in some thick sections	SEM	Present work
Polyethylene oxide (Polyox®) (1 wt %)	3 to 20	1.5 to 2.0	SEM	Present work
Polyvinyl alcohol (Elvanol®) (3.5 wt %)	0.1 to 0.3	Very thick	SEM	Present work

by relatively thin walls typical of the fibrillar structure. However, the structure of the gel is non-uniform in size as can be seen in Fig. 1f, and also by comparing Fig. 1a with Fig. 1b and Fig. 1c with Fig. 1d. The range of pore and wall dimensions are given in Table I.

As indicated by Fig. 1e the pore walls seem to have thin extensions, about 0.1 μm in thickness. Such extensions provide additional solid surface in the gel which can promote heterogeneous nucleation. The thin walls in this gel offer the advantage of yielding easily to the pressure of the growing crystal.

When the concentration of the dissolved monomer is raised from 2.5% to 4.0 wt% a noticeable change in the structure takes place (see Fig. 2). Even though the general features of the fibrillar structure still remain, the pore walls

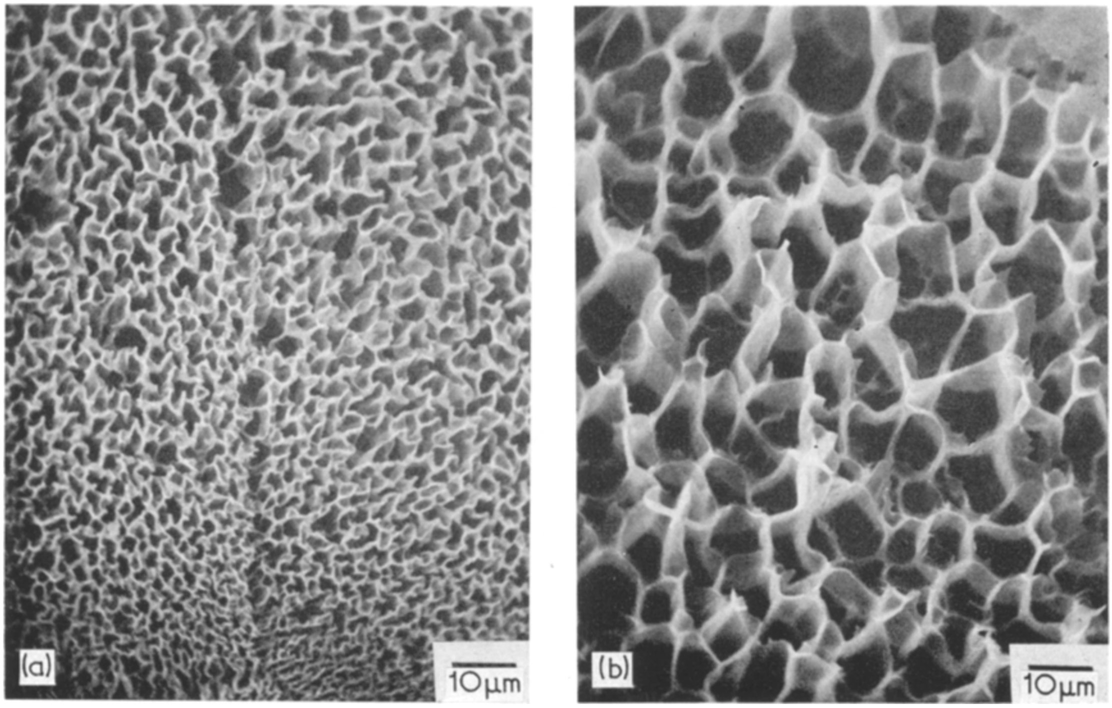


Figure 1 (a) to (f) Cyanogum 41®. 2.5 wt %.

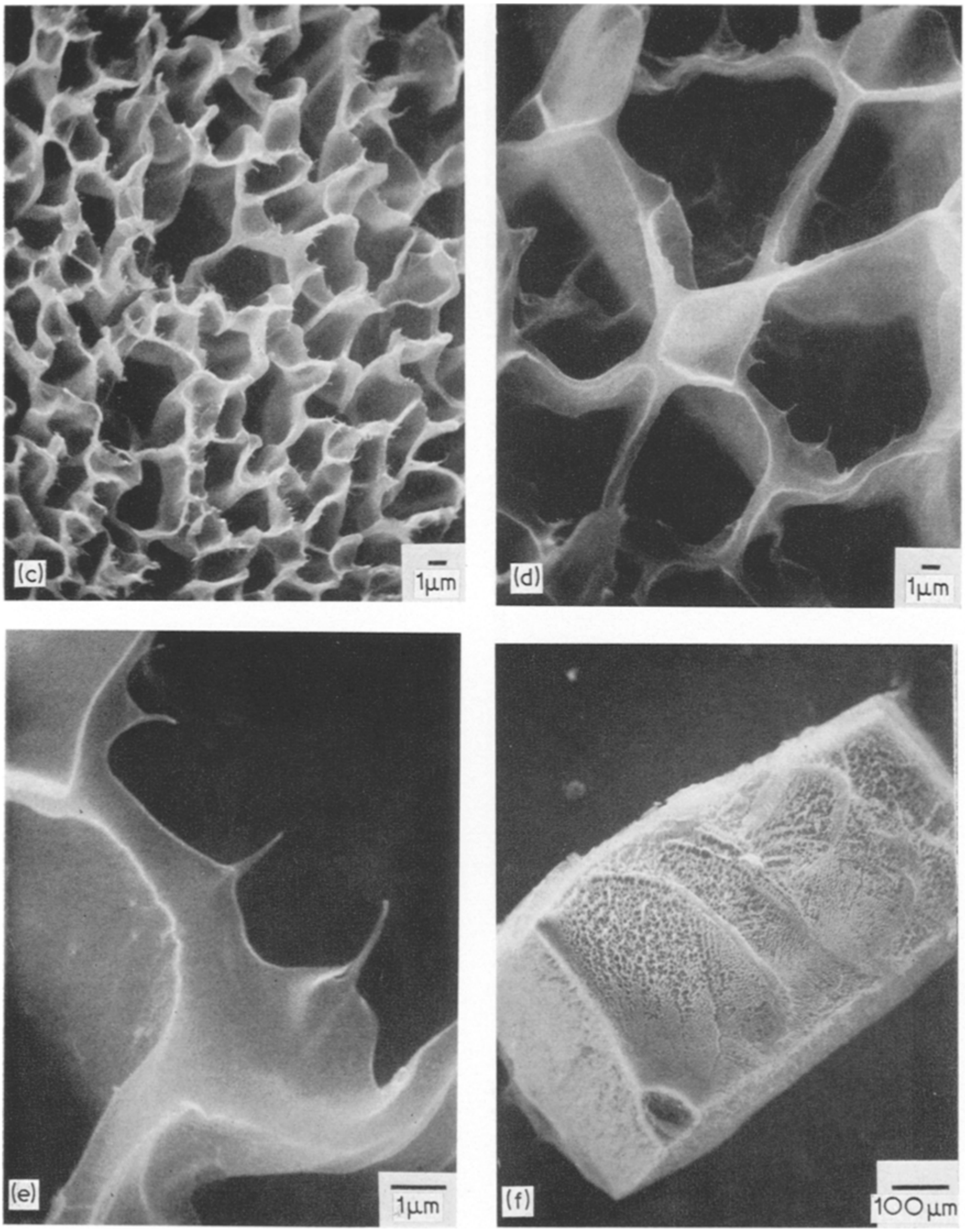
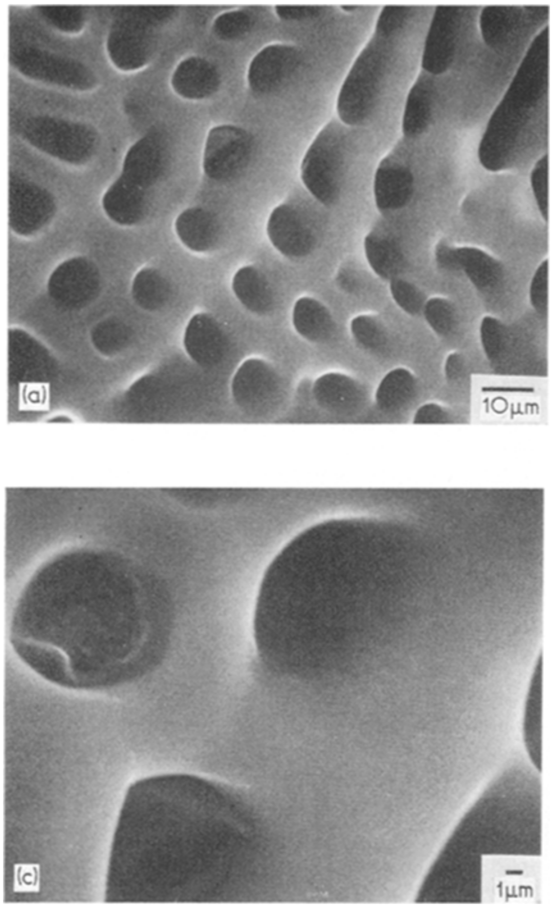


Figure 1 continued.

become much thicker relative to the pore diameter thereby decreasing the cross-sectional area available for diffusion of the electrolytes, (i.e. decreasing the diffusion rates). Since the



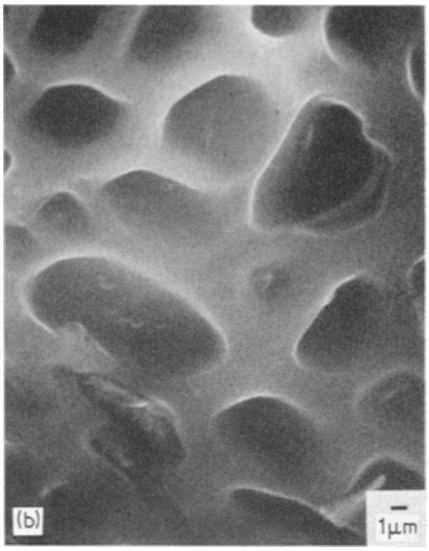


Figure 2 (a) to (c) Cyanogum 41®, 0.4 wt %.

number of pores per cross-sectional area decreases it follows that heterogeneous nucleation in such gels should decrease because of less available surface area for nucleation. This is in contrast to the observations made by Halberstadt *et al.* [19] who attributed the higher nucleation observed in silica gels prepared from 0.3 M Na_2SiO_3 solutions compared to gels prepared from 0.1 M Na_2SiO_3 solutions to the higher density of the gel. More likely, the higher nucleation in this latter case can be related to the higher concentration of sodium salt in the gel's liquid phase rather than to a variation in the gel's solid phase structure.

It is quite apparent that nucleation is associated not only with the structure of the solid phase but also with the structure of the liquid phase. Also, the gels observed in Fig. 2 are more likely to exert a higher pressure on the growing crystal, and thereby damage it than would the more dilute gels shown in Fig. 1.

Figure 3 Brushite crystals grown in Cyanogum 41® gel, 2.5 wt %.

Fig. 3 shows a typical crystal growth experiment conducted in Cyanogum 41® gel of 2.5 wt %. The crystal grown is brushite ($CaHPO_4 . 2H_2O$) and the experimental conditions other than the gel forming materials are similar to those reported by LeGeros and LeGeros [23]. The typical dendritic morphology of the grown crystals is more likely to result from the differences in the liquid phase of the gel (i.e. dissolved electrolytes) than from differences in the structure of the gel's solid phase.

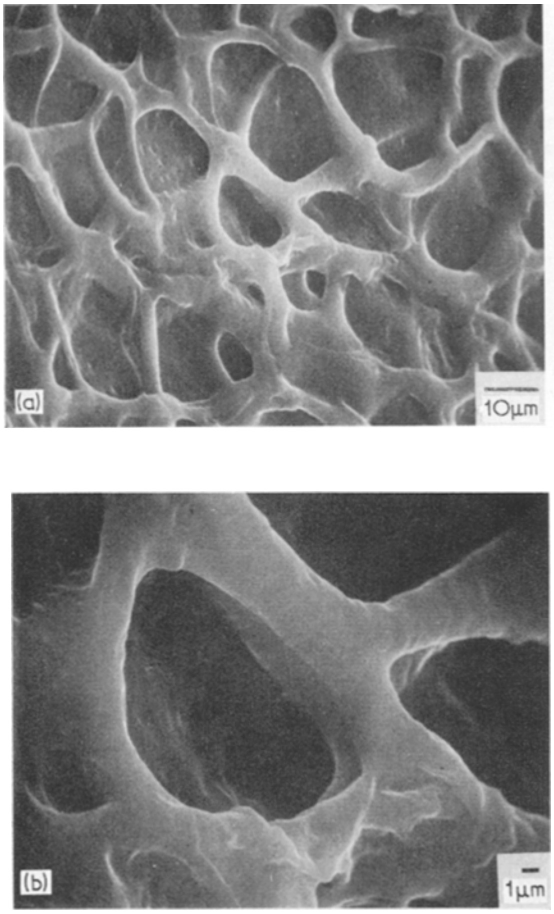


Figure 4 (a) and (b)Polyethylene oxide gel.

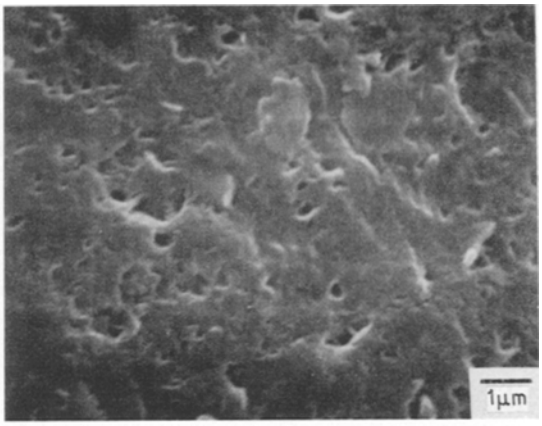


Figure 5 Polyvinyl alcohol gel.

Figure 4 depicts a typical structure of polyethylene oxide gel. Fig. 4a indicates that the wall thickness in the gel is quite uniform. This factor is important for the growth of good quality crystals because such a gel is likely to exert a more uniform pressure on the growing crystal.

It is noteworthy that the inner surfaces of the pores which are pitted, may induce higher heterogeneous nucleation due to an increased surface area. Fig. 4b clearly shows the inner structure of a typical pore with its twisting interconnecting channels.

Fig. 5 shows the structure of a polyvinyl alcohol gel. The micrograph indicates the very fine texture of the gel. This gel does not seem to possess a typical continuous fibrillar structure but rather a cellular character similar to the one manifested by basic silica gels as shown by Halberstadt [19]. Micellar structure has been suggested for junctions in Polyvinyl alcohol-water gels, which can be treated as the binary associations of free cross-linking sequences as proposed by Hirai [24]. In spite of the lack of direct evidence, the distinct difference between this gel and the previously described ones, may be attributed to a quicker gelation rate. Another possible explanation may be related to the initial polymer concentration in solution, since 3.5%, which is rather high, was the minimum concentration that resulted in a gel capable of supporting the top-solution placed on it.

5. Conclusions

The importance of the gel structure as effecting both the nucleation and growth processes has been discussed. The surface structure of the solid phase of the gel appears to be essential in determining the nucleation behaviour, rather than the density of the gel. Gels which exhibit the following properties seem to be good candidates as crystal growth media: continuous structure of both solid phase and liquid phase and sufficient degree of elasticity and mechanical yield to the growing crystals. It appears that polyacrylamide and polyethylene oxide gels satisfy the above requirements and as such appear to be promising as crystal growth media.

The effect of the structure of the liquid phase as influenced by both its proximity to the gel solid surface and its electrolyte contents has also been discussed.

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