

Slightly Crosslinked Poly(*N*-vinylcaprolactam) Gels as the Media for Growth of Copper(II) Sulfate Pentahydrate Crystals

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ABSTRACT: The behavior of slightly crosslinked poly(*N*-vinylcaprolactam) (PVCa) gels in a CuSO_4 solution in water and ethanol was studied. The investigation was carried out for PVCa gels with polymer contents of 4% and 7%. The effective absorption of CuSO_4 by PVCa hydrogel accompanied by gel shrinking was observed for the CuSO_4 aqueous solution. It was shown that dendrite crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ localized within the gel sample are obtained after placement of gels samples into ethanol. The crystal habit depends on gel concentration. It was found that slightly crosslinked PVCa gels are promising as media for the growth of crystals. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2838–2842, 2001

INTRODUCTION

The first investigations of gels as media for crystal growth were performed long ago,^{1–3} and until now it has remained one of the widespread methods for crystal growth.^{4,5} Crystal growth in the gel is, in fact, a particular case of solution growth in which the solution is trapped in a polymeric gel structure. Presence of the gel is responsible for special features of nucleation and growth.⁶

The feeding of the crystal surface during crystal growth in gels results from the solution's diffusion through the gel. The gel growth technique can be described as follows: Convection currents cannot occur in gels; thus, mass transfer is ensured only by diffusion. It was found that reagents can diffuse into the gel, but gels can only get rid of reagent excesses by dialysis.⁷ Monocrystals of Cu and Au were grown by Holms by diffu-

sion of the reductant into gel saturated with expedient salts.³ One way to get soluble crystals is crystallization induced by diffusion of a solvent in which the material is insoluble in gel. The diffusion of this liquid in the gel increases the supersaturation and induces crystallization.⁸ The gel growth method makes possible the growth of rather large-size crystals of good optical quality as compared with crystals obtained by crystallization from free solution.^{9,10}

Gel structure influences the crystal growth at every step of the crystal formation. One of the most important functions of the gel is establishment of a concentration gradient distribution. In addition, gel works as a “three-dimensional crucible,” with the gel phase supporting the growing crystal and simultaneously feeding it with reagents for crystal growth without directly influencing the growing face of a crystal. So the gel growth technique has some advantages.

In most previous works on this topic, physical gels were used as media for crystallization. Physical gels, such as agarose and gelatine, are gels obtained by hydrogen bonding and van der Waals interactions.⁷ The gelation of these gels depends

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on such physical parameters as temperature or pressure, and the sol–gel transition is reversible.

In the present work we studied crystal growth in covalently bonded, slightly crosslinked gels of poly(*N*-vinylcaprolactam) (PVCa). This gel seems well suited as a medium for crystal growth. In fact, PVCa is a nonionic synthetic polymer soluble both in water and in organic compounds. This property can be used for the growth of soluble crystals that can make use of the variation of solubility by the addition of another solvent. PVCa has a high complex-formation ability^{11,12} that is explained by the amphiphilic character of the monomer unit. The types of interaction between the macromolecule and the low molecular substance leading to the complex formation can vary (for example, electrostatic, van der Waals interaction, hydrogen bonding).

The purpose of the present work was the investigation of slightly crosslinked gels of poly(*N*-vinylcaprolactam) as media for crystal growth, using CuSO_4 crystals as an example.

EXPERIMENTAL

Gel Preparation

Gels were obtained by radical polymerization of *N*-vinylcaprolactam in ethanol solution with the crosslinking agent *N,N'*-methylene-bis-acrylamide (1 crosslinker per 100 monomer molecules) and with the initiator 2,2'-azobis(2-methylpropanitrile). The initial content of *N*-vinylcaprolactam (VCa) was 50% or 70%. The solution was transferred to 5-mm diameter glass tubes, and argon was bubbled for 10 min to remove oxygen. Then the tubes were sealed and placed into a thermostat. Polymerization was carried out at 58°C for 2 days. Then the gels were removed and washed with distilled water for 2 weeks.

For the determination of polymer content of the gel we used the parameter β , which is the weight ratio of dried polymer network to polymer network swollen in pure water at 20°C (expressed in percent). For the obtained gels, the dried polymer-content β was 4% for the gel with an initial VCa content of 50% and 7% for the gel with an VCa initial content of 70%.

Photometric Measurements

The content of the copper ions in aqueous solution was evaluated by photometric measurements per-

formed in the presence of ammonium, according to a procedure described elsewhere.¹³ Photometric measurements were performed at a Hewlett-Packard 8452A spectrophotometer. The solutions were measured in 1-cm quartz cells at a wavelength interval of 200–800 nm. The pure water was measured as blank solution. The concentrations of CuSO_4 inside the gels (C_{in}) were estimated from the differences of the CuSO_4 concentration in the external solution.

$$C_{in} = \frac{(C_0 - C_{ex})V_s}{V_g}$$

where C_0 is the initial concentration of CuSO_4 in the external solution, C_{ex} is the concentration of CuSO_4 in the external solution after immersing the gel, V_s is the volume of the external solution, and V_g is the gel volume.

Microscopy

The crystals obtained inside the gels were investigated by transmitted light with an MIN-8 polarization microscope (LOMO, Leningrad, Russia).

X-ray Diffraction

The type of crystals was determined by comparison of experimentally measured distances between planes with known reference data.¹⁴ Distances between planes were determined by X-ray analysis of powder measured for Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). X-ray analysis was carried out on an DRON-2.0 X-ray diffractometer.

RESULTS AND DISCUSSION

First, the behavior of PVCa hydrogel in CuSO_4 aqueous solution was studied. Gel samples were immersed into CuSO_4 solutions of fixed concentrations that varied from 0.05 to 0.42 mol/L and kept in the solutions at room temperature for a week. Then the gel samples were weighed, and concentrations of CuSO_4 in the external solution were measured by the spectrophotometer. The concentrations of CuSO_4 inside the gel were estimated from the variation of the CuSO_4 concentration in the external solution. Figure 1 shows the dependence of the relative change of gel mass (m/m_0) in the CuSO_4 (curves 1 and 2) solution and the ratio of equilibrium CuSO_4 concentrations in-

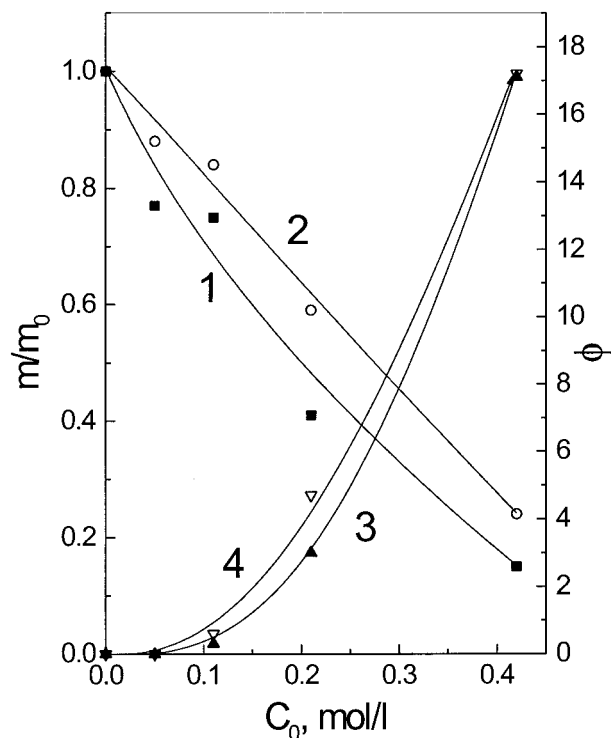


Figure 1 Dependence of the relative mass change (m/m_0 ; curves 1 and 2) and the ratio of CuSO_4 concentration within the gel to the equilibrium CuSO_4 concentration in the external solution (ϕ ; curves 3 and 4) on the initial CuSO_4 concentration in the external solution (C_0). PVCa content within the gel is 4% for curves 1 and 3 and 7% for curves 2 and 4. The m represents the weight of PVCa gel swollen in CuSO_4 aqueous solution and the m_0 the weight of PVCa gel swollen in water.

side and outside the gel (ϕ) (curves 3 and 4) on the initial CuSO_4 concentration (C_0).

It can be seen that after immersing of the PVCa gel in the CuSO_4 solution, CuSO_4 molecules concentrate inside the gel (the value of ϕ is well above unity). In this case gel contraction takes place. The contraction of polymer gel in the presence of salt can be explained by (1) creation of additional bonds as a result of complex formation of Cu^{2+} ions and amide groups of PVCa chains and (2) increasing hydrophobic interactions as a result of water structure changes in the presence of salt ions.¹⁵

The next step in the present work was placement of the CuSO_4 -bearing hydrogel samples that had been prepared from immersing PVCa gel in CuSO_4 solution (the concentration of CuSO_4 inside the gel was about 0.6 mol/L) into 97% ethanol solution. The high saturation necessary for crys-

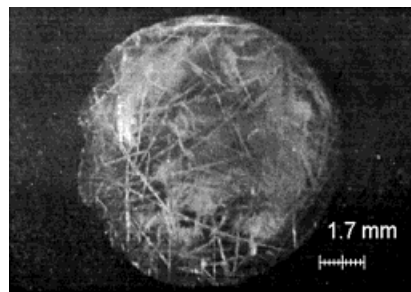


Figure 2 Photograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals within 4% poly(*N*-vinylcaprolactam) gel.

tal growth in the gel phase arises from ethanol diffusion into the gel but water diffusion from the gel into the external solution. CuSO_4 is well soluble in water (203 g/L, or 1.3 mol/L, at 20°C) and is more poorly soluble in alcohol (11 g/L, or 7×10^{-2} mol/L, at 25°C).¹⁶ PVCa gels with polymer contents of 4% and 7% were investigated. After immersion of the CuSO_4 -bearing PVCa hydrogel samples of both polymer concentrations in ethanol solution at room temperature, growth of dendrite crystals localized within the gel sample was obtained after one day (Fig. 2).

The gel samples with crystals inside them were then examined with a polarization microscope. Small crystals can be seen on each dendrite needle (Fig. 3). The analysis of crystal habit and measurement of angles of crystal tables allows the conclusion that these are $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals.¹⁷ However, the obtained substance should be also analyzed directly by X-ray methods since double salts and hydrated substances are often obtained.⁷ In this case two different modification of CuSO_4 crystals can be formed.¹⁸ To confirma-

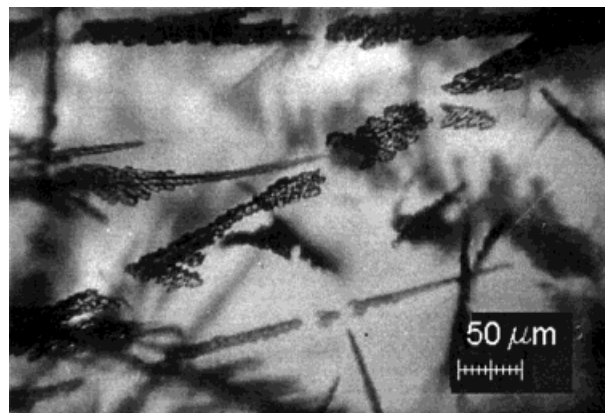


Figure 3 Photograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dendrites within 4% poly(*N*-vinylcaprolactam) gel.

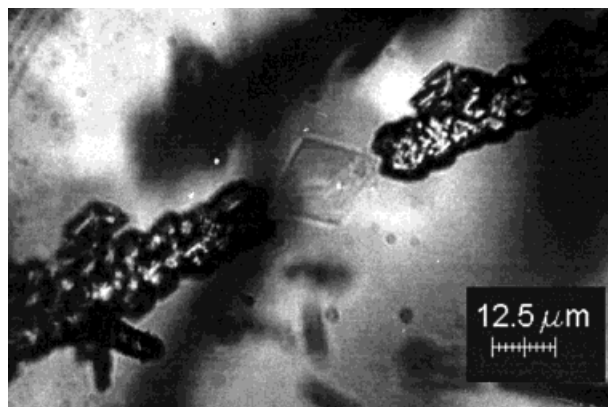


Figure 4 Photograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals within 4% poly(*N*-vinylcaprolactam) gel.

tion the conclusion that there was $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ formation, powder of the reduced fine particles of crystal together with dried gel were investigated by X-ray diffractometry. The type of crystal was determined by comparison of experimentally measured distances between planes with known reference data.¹⁴ This analysis confirmed that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals are obtained in gels.

It is known that dendrites can be grown after the addition in a saturated aqueous solution of a solvent in which the material is insoluble (e.g., ethanol or acetone).⁷ Therefore, the growth of dendrite crystals within the gel saturated by CuSO_4 aqueous solution and immersed in ethanol solution can be caused by the production of the saturated CuSO_4 solution inside the gel. During this process the CuSO_4 molecules remain in the gel phase and do not diffuse into the external solution.

To compare the character of crystal growth in the solutions and in the gels, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystal growth experiments in the solutions were also carried out. The ratio of ethanol to the CuSO_4 aqueous solution was the same as in the experiments with gels. Analysis of the grown crystals shows that dendrite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals are also obtained in the solution, but crystals grown inside the gel have many features related to the influence of the gel media.

Figures 2–5 show photographs from a polarization microscope of crystals grown in 4% and 7% PVCA gels. It can be seen in Figure 3 that there are small planes of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals on any needle. This phenomenon is not observed for needles in the solution. The growth of these crystals can be explained by taking into account the deceleration of diffusion process in the gel. At the

first stage of growth the needle was fed by the nearest growth substance. During growth the feed substance was exhausted and because in gel the diffusion rate is lower than in the solution, the new feed substance input was made difficult, and the needle growth discontinued. As a result of this process the CuSO_4 concentration gradient developed, leading to the diffusion of the CuSO_4 molecule toward the needle and the subsequent growth of plate crystals on the needle as on the substrate. This phenomenon does not occur in the solution in which there are convection flows and all the feed substance is spent during needle growth. In addition to crystals growing in gels, the phenomena of break of needle growth by the growth of plate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ monocrystals (Fig. 4) occurred. These phenomena were not observed for crystals grown in the solution. It is interesting to note that after the break the needle growth continues in the same direction. There can be several breaks on one needle. This can be explained by the heterogeneity of the polymer network in the gel: some lacunas with polymer chains of a smaller density can occasionally be formed inside the gel. The crystal growth in these lacunas is not influenced by the network, and consequently the growth occurs in all the directions, not just in the more advantageous direction as the needle crystals do. The maximum thickness of this monocrystal was estimated by optical observation under a polarization microscope at crossed Nicols.¹⁸ The crystal's thickness turned out to be about of 7 μm .

For a better understanding of network influence on crystal growth in the gel phase, gels with polymer contents of 4% and 7% were studied. It was found that dendrite crystal growth occurs at both concentrations. Two types of dendrite crys-

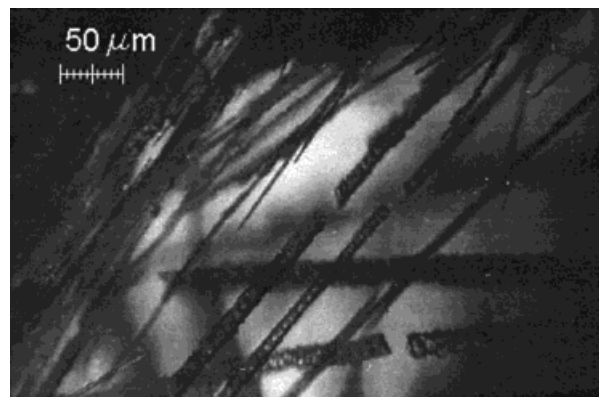


Figure 5 Photograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dendrites within 7% poly(*N*-vinylcaprolactam) gel.

tals were recognized during the comparison examination of habit of crystals grown in gels with the two polymer concentration (Figs. 3 and 5). The absence of dendrite branches in the more dense 7% gel indicates the existence of a decrease of material input toward the growing crystal as compared to the material diffusion toward the same surface in the less dense 4% gel. All the above-listed crystal growth features occur both for 4% and for 7% gels. However, growth of smaller-sized planes can be observed with the 7% gels as compared to the 4% gels. This fact can be associated with the higher polymer concentration of the 7% gel (Fig. 5). Therefore, in the more dense gel crystal growth is influenced by the network.

CONCLUSIONS

The present work shows that chemically crosslinked PVCa gels can be used for the crystallization of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals under specified growth conditions, which were elaborated in this article. It was found that the crystal habit depends on gel density. In particular, this dependence can be used to examine the homogeneity of synthesized gels.

We studied the crystallization of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a model compound for crystal growth in PVCa gels. Because PVCa is a biocompatible polymer, PVCa gels seem to have applications as media for the crystallization of more complicated organic compounds including proteins and drugs used in pharmacology and medicine.

In conclusion, it is important to emphasize some advantages of using chemically crosslinked polymer gels as crystallization media over using commonly used physical gels: (1) external condition changes do not lead to gel disruption; (2) it is possible to use the "intelligent" gels (for which changes of external conditions such as temperature and pH lead to changes in the conformation state of the gel), which provide an easy way to vary the crystallization media properties; and (3) crosslinked gel samples can be easily moved mechanically from one solution to another.

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