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ORIGINAL CONTRIBUTION

Self-assembly and solid-state photo polymerization of acrylamide crystal film

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Abstract Solid-state polymerization has many advantages such as solvent-free, environmental friendly, less cost, and high purity of product. In this study, a crystal film of polyacrylamide was synthesized by solid-state polymerization. Firstly, gelatin was used for inducing acrylamide to form monomer crystal film through self-assembly in an aqueous solution. Then, the monomer crystal film underwent a photo-initiating polymerization to give the corresponding polymer crystal film. The structure of the crystal film was confirmed by Fourier-transformed infrared spectrometry, X-ray diffraction, microscopic melting point detector, and differential scanning calorimeter. The morphology was observed with scanning electron microscopy. The molecular weight was measured by gel permeation chromatography. It was found that a well-organized polyacrylamide crystal film was formed by controlling the synthetic conditions. The lattice size of the crystal changed very little before and after polymerization. The crystal film displayed a fibrous shape and was well-organized.

Keywords Solid-state polymerization · Crystal film · Self-assembly · Acryalmide

Introduction

Polyacrylamide is a common water-soluble polymer which has wide applications in industry. Polyacrylamide (PAM) and its derivatives are conventionally prepared in solutions with methods of solution polymerization, suspension, and emulsion polymerization. However, the conventional synthetic methods cause many problems. For example, it requires a lot of solvents which results in environment pollution, and the synthetic procedure is complicated, and it consumes too large amount of energy.

To overcome these problems, some people use a solid-state polymerization (SSP) method with which monomer molecules are polymerized in a solid state. Solid-state polymerization has aroused widespread interests of scientists due to its advantages such as solvent-free, environmental friendly, low active energy, non-inducing period, less cost, high purity of product, and the controllable structure. There are some reports on SSP reaction induced by light irradiation [1–3]. Various polymers such as poly(methacrylamide) [4] and poly(dimethacrylate) [5] were obtained by SSP. There have been also some reports on solid-state polymerization of acrylamide. But the reported products of polyacrylamide were amorphous, a few products were obtained in crystalline state [6]. To solve the problem, developing a new technology for preparation of polyacrylamide is significant and greatly desirable. Polymerization accompanied by the self-organization has attracted researcher's attention to develop organic nanoparticles [7] and synthetic metals [8]. Sometimes, the cooperative self-assembly in the polyelectrolyte system induced to form a regularly organized structure. In our previous work, we synthesized poly(2-acrylamide- 2-methylpropane sulphonic acid) (PAMPS) by solid state polymerization in complexation of PAMPS with gelatin [9] and obtained the giant spherulites PAMPS.

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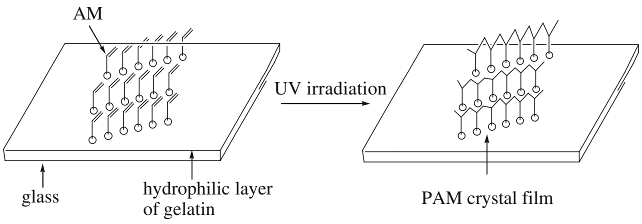


Fig. 1 A scheme of the preparation of polyacrylamide crystal film

In this study, we have approached a unique technology to synthesize crystalline polyacrylamide. The monomer crystal film of acrylamide is formed through self-assembly at the presence of gelatin in aqueous solution, and then the crystal acrylamide film is polymerized by photo initiation in solid-state. The preparation and characterization of the crystal film are investigated.

Experimental

Materials and instruments

Acrylamide (AM), gelatin (GN), polyvinyl alcohol (PVA), and polyethylene glycol (PEG) were purchased from Medical Group of Shanghai; 2-hydroxy-2-methyl- 1-phenyl-1-acetone (HMPA1173) was purchased from Ciba company. AM was recrystallined from ethanol, and the others were used as received.

Fourier-transformed infrared spectrometry (FTIR, FTLA 2000-104, America); differential scanning calorimeter (DSC822^e, Switzerland); UV-bis spectrometer (TU-1901 Beijing); gel permeation chromatography (GPC) Agillent-1100ilent, America; scanning electron microscope (SEM, Quanta-200); UV-curing machine, UV2, 80 W/cm high pressure mercury lamp; Wide-angle X-ray diffraction (WAXD, Ni-filtered Cu Kα (λ=0.154 nm), RINT 2000, Rigaku; X_4 microscopic melting point detector, Beijing third Optical Instrument Company.

Preparation of polyacrylamide crystalline film

Gelatin, a water-soluble polymer, was dissolved in deionized water to form an aqueous solution with particular concentration. A certain amount of AM and small amount of photo-initiator (HMPA1173) were added into the solution and mixed evenly. The mixture was put on a glass by drooling after expelling bubbles at a reduced pressure. With the evaporation of solvent, a crystalline AM monomer film was formed close to gelatin on the surface. The monomer film was regularly arranged in a crystalline form on the glass. The crystal film was placed in a UV radiation-curing system for photo-initiating polymerization. Finally, a crystalline polyacrylamide (PAM) film was prepared. The scheme of the preparation was showed in Fig. 1.

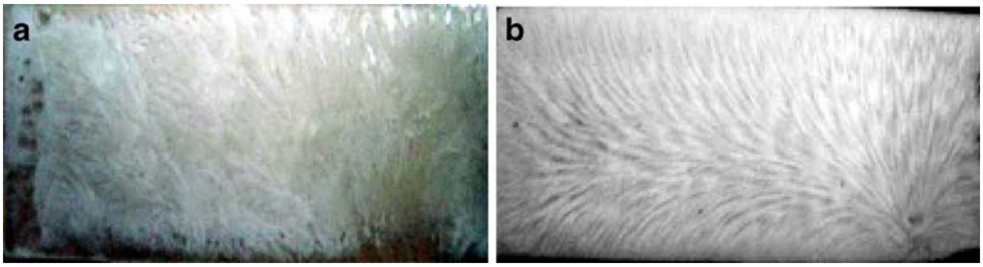
Results and discussions

Effect of the adding polymer types on the self-assembly of acrylamide

Three different water-soluble polymers, polyvinyl alcohol (PVA), polyethylene glycol (PEG) and gelatin, are used for inducing self assembly and crystallization of AM, respectively. PVA is a good water-soluble polymer due to a large number of chain-side hydroxyl groups. It is found that, in most cases, acrylamide can form a crystal at the presence of PVA, and the crystal acrylamide is precipitated as the solvent volatiles. However, the acrylamide crystal film is a loose string, and it is not very uniform, flat, and dense-spelled crystal. (Fig. 2a). Additionally, it takes a long procedure for PVA to be dissolved in water, and the solubility is low. Thus, PVA is not an ideal candidate polymer for assisting the self-assembly and crystallization of AM. When using polyethylene glycol (PEG) as an assisting polymer, we observe that no crystal acrylamide is formed.

Gelatin is a peptide polymer obtained through part hydrolysis of collagen from animal skin, bone and other organizations. Gelatin-type substances have many excellent physical and chemical properties. The plenty of hydrophilic groups (COOH, OH) in the molecules and good film-formation ability make gelatin a satisfactory polymer for assisting self-assembly and the crystallization of acrylamide. The results indicate that as long as gelatin is mixed with acrylamide in an appropriate ratio in aqueous solution, a very homogeneous, flat, compacting-spelled single AM crystal film will form with the volatility of the solvent (see Fig. 2b).

Fig. 2 The morphology of AM crystal film on PVA (**a**) and on GN (**b**)



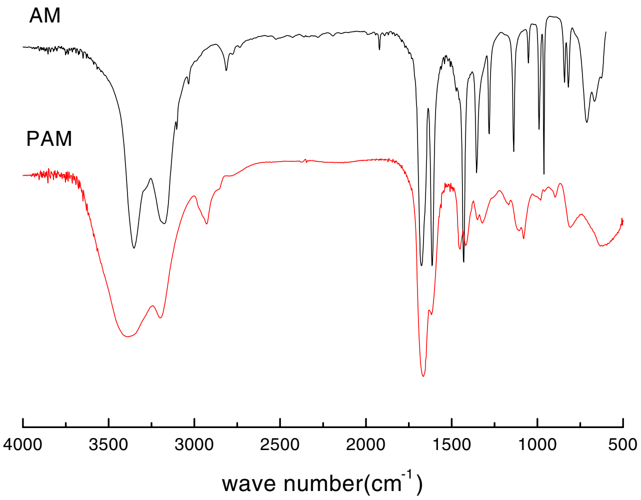


Fig. 3 The FTIR spectra of the crystal films of AM and PAM

Effect of the concentrations of gelatin and AM on the morphology of the crystallization

According to the analysis above, gelatin is a desirable substance for self-assembly of AM. So, gelatin is chosen as the assisting polymer, and the effect of concentrations of gelatin and AM on the crystal morphology is investigated. We have observed that at a fixed gelatin concentration (10 wt.%), with the increase in AM levels, the surface morphology of the crystal gradually varies from osteoporosis to dense (Fig. 3a–c). When the weights of gelatin and AM are equal, the crystal displays leaf shape. The fibrous "veins" grows along the center line on both sides (Fig. 3a). When the AM content is twice that of gelatin, the surface morphology is "bird plumes"-shaped (Fig. 3b). With the continuous increase in AM up to triple of GN, a very homogeneous and dense-spelled AM monomer crystal film is observed. The crystal is ordered regularly to form a perfect crystal film (Fig. 3c). However, when the gelatin concentration is 20 wt.%, the crystallization of the film is not easy. No crystal is observed (Fig. 3d). It is explained that in a certain range of gelatin concentration (e.g., 10%), AM molecules are able to arrange in some regular ways through hydrogen-bonding interactions between AM and gelatin, producing various crystal morphologies with the change of AM contents. However, if the gelatin is too concentrated (e.g., 20 wt.%), on one hand, the hydrophilic groups of gelatin are difficult to be arranged in a regular way due to the entanglement of the polymer chains; on the other hand, the viscosity of the solution increases, which obstructs dispersion of AM molecules. Both reasons cause disorder of the AM molecules.

FTIR analysis

The FTIR spectra of the monomer AM and crystal film of PAM are showed in Fig. 4. We can see that the peak 1,614 cm^{-1} of the unsaturated double bond in acrylamide monomer disappears. The bending vibration (960 cm^{-1}) of C–H near the carbon double bonding no longer existed. It is concluded that the AM is polymerized through light initiation.

Polymer yield analysis by UV spectrometry

To examine the content of polymerization of AM crystal film, the polymer yield is analyzed by UV-vis spectrometer. The sample of the polymer crystal film is broken to become small powder which is immersed in certain amount of ethanol for 2 h since monomer AM is soluble, but polyacrylamide is insoluble in ethanol. The concentration of the extracted AM is determined by UV spectrometry followed by calculation. The percentages of AM residual in the crystal film are listed in Table 1.

It is obviously seen that the percentage of AM in the film decreases as the irradiation time increases. Eight minutes later, the AM residual changes very little for the further irradiation. Based on the results, we keep the irradiation time for 8 min in our experiments.

Fig. 4 The morphologies of AM crystal films with various AM and GN concentrations (**a**, **b**, **c** GN%=10 wt.%, GN: AM=1:1, 1:2, 1:3, respectively; **d** GN%=20 wt.%, GN:AM=1:2)

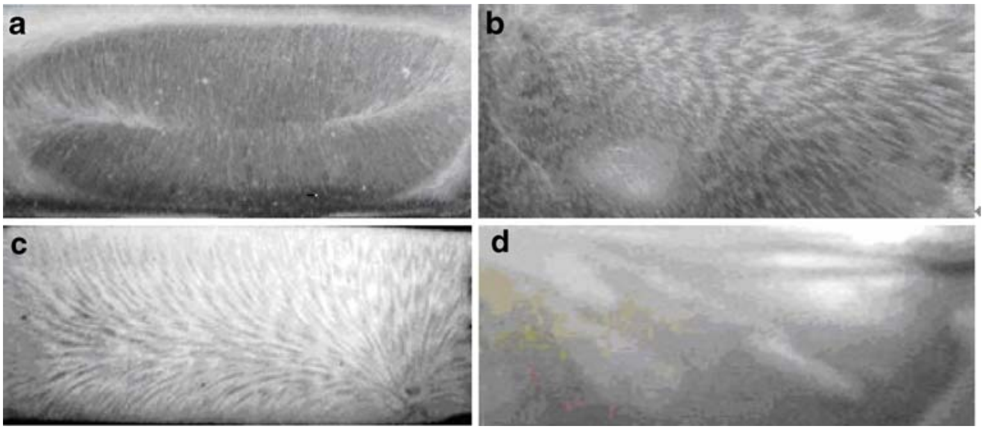


Table 1 The AM residual in the polyacrylamide crystal film[a]

UV irradiation time (min)	AM in the film (wt.%)
2	0.302
4	0.255
6	0.098
8	0.050
10	0.048
15	0.047

[a] The sample is from Fig. 3c

GPC analysis

Effect of photo-initiator content on molecular weight

Figure 5 shows the influence of photo-initiator HMPA 1173 content on the molecular weight of the polymer. The initiator concentration is with respect to the total amount of the monomer. It is observed that the molecular weight increases with the increase in the photo-initiator. This trend is opposite to conventional free radical polymerization. The reason may be that the polymerization is carried out in a solid-state; the radicals are not able to move freely in the reaction system. If the concentration of the photo-initiator is low, the polymerization is easily terminated through chain transfer due to some defeat of the monomer crystal. Therefore, the polymer formed usually has low molecular weight. However, if the concentration of the initiator is high, more radicals can be evenly dispersed in the monomer. Consequently, there are more long radical chains in the system. The chance for coupling termination increases which causes high molecular weight. But the study indicates that initiator needs to be controlled a certain degree. This is because the initiator HMPA 1173 is oil-soluble; the increase of initiator will inevitably need to add more solvent for emulsification, which will negatively affect the morphology of the crystal film. Our experiment result indicates that 0.8 wt.% of the initiator is appropriate.

Effect of irradiation time on molecular weight

The irradiation time also affects the molecular weight of the polyacrylamide crystal film. Figure 6 shows the molecular weight dependence on irradiation time at a fixed value of the initiator (0.8 wt.%). As can be seen from Fig. 6, with the increase of irradiation time, the molecular weight raises from 10,900 (2 min irradiation time) to 24,500 (8 min irradiation time) and then declines. Probably, it is because the too long irradiation time may result in degradation of the polymer. In addition, over-irradiation time will cause a yellow color polymer. So, controlling the optimal irradiation time is essential for obtaining good quality products.

X-ray diffraction analysis

Figure 7 is the X-ray diffraction curves of crystals AM and PAM. The diffraction peaks further prove the formations of the crystal AM and PAM in this study. Monomer AM belongs to monoclinic system. The symmetry of PAM crystal lattice is not high (usually three ramps or monoclinic systems). Comparing to monomer AM, the number of diffraction peaks of PAM obviously decreases. Figure 8 shows the major corresponding diffraction angles (2θ) and distance of crystal face (Å) for AM and PAM. It is seen that there is very little difference in the distance between AM and PAM. This indicates that the crystal lattice of AM changes very little before and after irradiation. Table 2 gives the sizes of

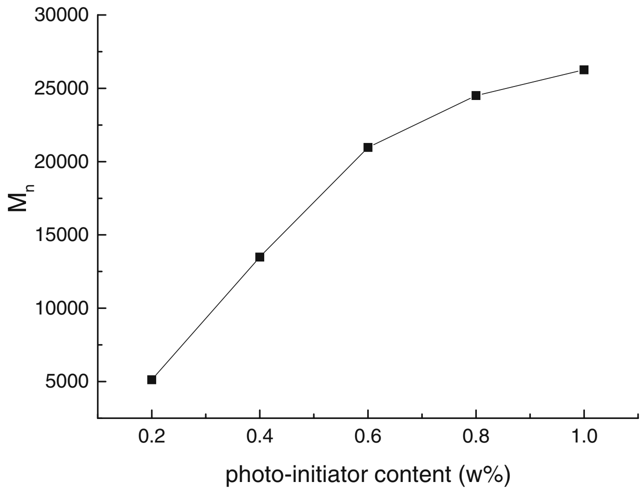


Fig. 5 Dependence of molecular weight on photo-initiator content (irradiation time: 8 min)

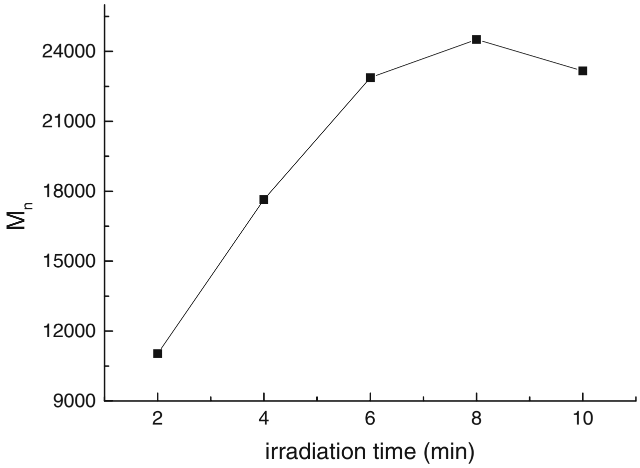


Fig. 6 The relationship of irradiation time and molecular weight

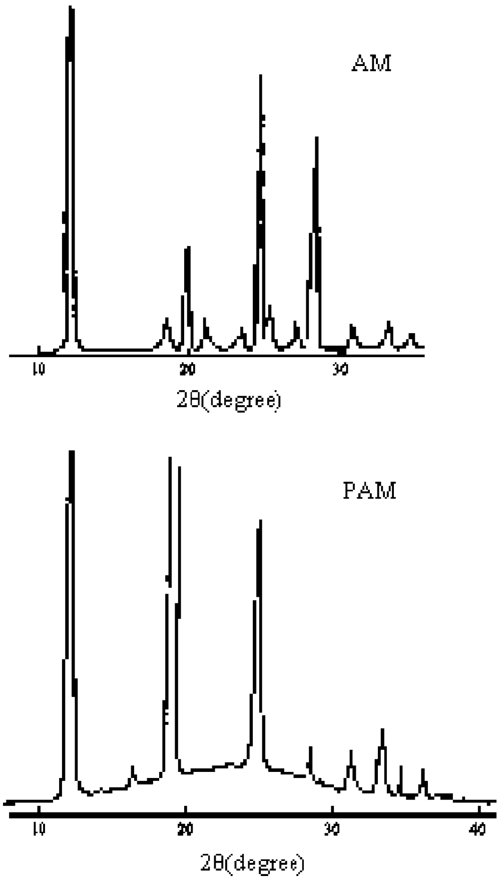


Fig. 7 X-ray diffraction diagram of crystal films AM and PAM

crystalline grain calculated based on the major diffraction peaks and according to Scherrer formula:

$$D_{hkl} = kl/\beta_{hkl} \cos \theta \qquad (1)$$

where D_{hkl} stands for the distance in the direction of perpendicular to the crystal face (hkl); k is a constant; β_{hkl} is the reflective (hkl) half width; λ is the incident wavelength of the X-ray; θ is the diffraction angle. The calculated results show that the micrograin sizes are small, in hundreds of Angstroms.

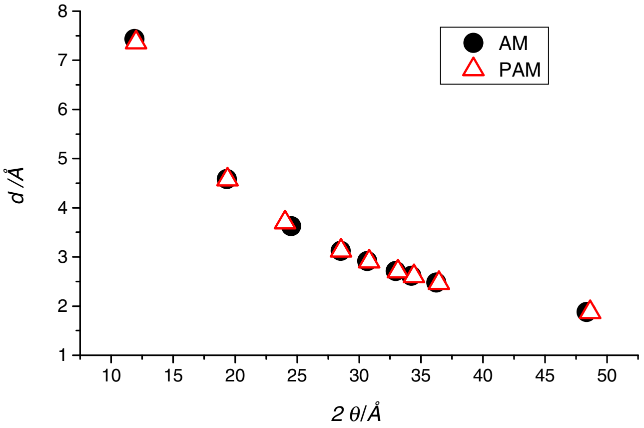


Fig. 8 Diffraction angle 2θ and the corresponding crystal face distance for AM and PAM

Table 2 Lattice sizes of the crystalline grain PAM

2θ (degrees)	β (radians)	D (Å)
12.009	0.00262	526.6
19.388	0.00227	613.0
24.042	0.00349	401.6
33.130	0.00349	409.8

Measurements of melting points of the crystals

Microscopic melting point detector is used to measure the melting points of the crystal AM and PAM films for further characterization of the crystals. Thus 0.1 mg of the sample is placed inside two slides of the instrument for the measurement at a heating rate of 5°C/min. The melting behavior is recorded in Table 3.

The purchased commercial AM has melting points between 83 °C and 88 °C. In this case, the melting point of our sample is 86°C. But the filmed crystal AM has a slightly increased melting point, 88 °C. It is because the filmed crystal AM is formed on the surface of gelatin. Through the induction of gelatin, the substance is denser, the interaction among the AM molecules is stronger, and the crystal structure is more perfect. All of the reasons result in the increase of the melting point. Table 3 displays that there is no fixed melting point for the filmed crystal PAM, and the melting process is a temperature range which is significantly higher than that of monomer AM. This is due to the defects of the polymer crystals. It is also observed from Table 3 that the filmed crystal PAM prepared at different irradiation time shows the varied temperature range for melting. The sample obtained through 2 min irradiation time starts to melt at 190°C and stops the melting at 250 °C. The melting points are lower than those of the samples obtained at longer irradiation time. It is

Table 3 The measurement of melting behaviors of the crystals

Samples	Melting points and process
Monomer AM	86 °C
Filmed crystal AM	88 °C
Filmed crystal PAM (2 min)[a]	190 °C edge melting, 250 °C crystal disappears
Filmed crystal PAM (6 min)	240 °C edge melting, 280 °C crystal disappears
Filmed crystal PAM (8 min)	240 °C edge melting, 290 °C crystal disappears

[a] It refers to the irradiation time for preparation of the PAM

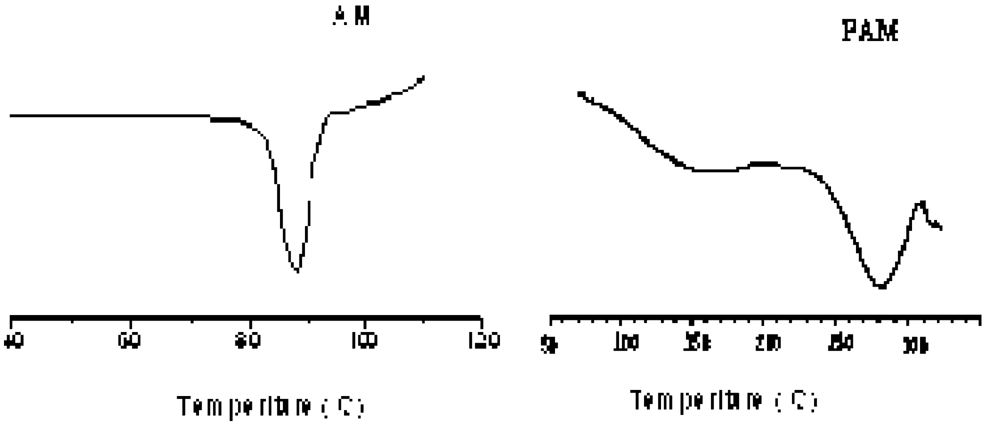


Fig. 9 The DSC curves of the crystal films of AM (**a**) and PAM (**b**) (speed of temperature increase: 5 °C/min)

explained that the sample obtained at less irradiation time has lower molecular weight than those of the samples obtained at longer irradiation time.

Differential scanning calorimeter characterization

Figure 9 represents the curves of differential scanning calorimeter (DSC) for the crystal films of AM and PAM, respectively. It is seen that there is a sharp endothermic peak in 88 °C, which indicates the melting point of AM (Fig. 9a). After irradiation, the monomer transforms to polymer, the single melting point peak disappears; instead, a new wide endothermic peak around 240~300 °C has emerged (Fig. 9b). This wide peak indicates the melting point of the PAM. The melting point of PAM is higher, and the melting temperature range is wider than that of monomer AM, which demonstrates the difference between polymer and monomer crystals. The DSC result corresponds to the measurement of microscopic melting point detector. This characterization provides more evidence for the formation of the crystal PAM.

Scanning electron microscope analysis

The scanning electron microscope is frequently used for the observation of the surface morphology of a polymer. Figure 10 is a SEM image of the crystal film PAM (8 min irradiation). We have observed that crystalline state PAM assumes the fibrous orientation distribution, and the arrangement is neat and denser. The image reveals that the crystal film PAM prepared in this study demonstrates a regular surface morphology.

The principle of the formation of crystal film induced by gelatin

The polymerization of AM adopts a free radical polymerization mechanism. The structure units of the polyacrylamide are mainly in a head-to-tail connection way. The geometry arrangement of polymer molecules may decide whether the polymer is in a crystalline state or amorphous state. Three-dimensional neat molecular chains are playing the decisive role for its crystallinity. Crystalline polymer cannot be obtained with a conventional solid polymerization method, since a monomer molecule must move to a certain distance to be able to link to another molecule for chain propagation. This will produce big strength which may destroy the monomer crystal lattice [10].

In the present study, the AM is mixed with gelatin in aqueous solution and then spreads out on a glass. Based on the difference of the physical properties such as density, surface tension, and polarity, gelatin takes priority to concentrate on the glass. The driving force for the self-assembly of AM is hydrogen bonding between amide groups of AM and hydrophilic groups of gelatin. The AM and gelatin produce strong hydrogen bonds through interactions among the polar groups (COOH, OH, NH_2). Along with the volatility of the solvent, the AM molecules are able to arrange regularly on the gelatin by self-assembly. In our previous work, we prepared PAMPS crystal with the same

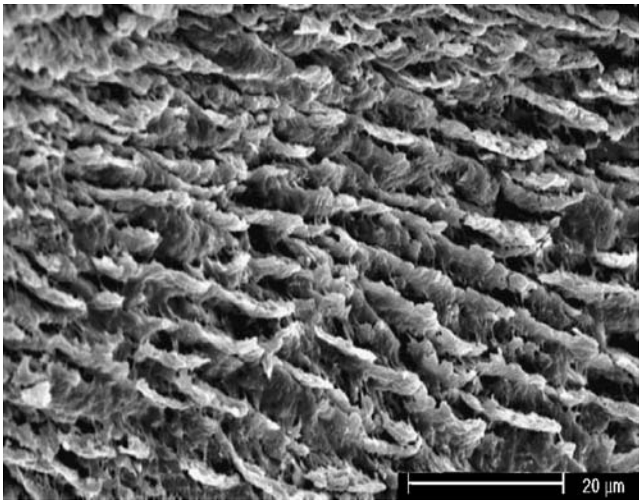


Fig. 10 The SEM image of the PAM crystalline film

method [9]. By comparing the two studies, it is observed that the self-assembly is less affected by charges in the monomers. When the monomer crystal film is irradiated for polymerization, the AM molecules only make a small adjustment to react with their neighboring molecules for the growth of the polymer chain. The reaction heat may be use for "activation" of the next member, favoring the continuous polymerization. The propagation of the polymer chain is controlled within the lattice; therefore, the crystal lattices change very little in the process from monomers to polymers, which is confirmed by X-ray diffraction.

Conclusion

A highly ordered three-dimensional neat crystal film of polyacrylamide can be prepared through self-assembly of the AM monomers induced by gelatin, followed by photo-initiating polymerization in a solid state. The selection of inducing polymer is essential for the formation of AM crystal. Gelatin demonstrates the better inducing property compared to polyvinyl alcohol and polyethylene glycol. When the feed ratio of gelatin and acrylamide is appropriate, the crystal film obtained is well-organized. This study provides a novel method for preparing the highly regular PAM crystal in solid state.

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