

# Graft Copolymerization of *N*-Vinylpyrrolidone onto Gelatin

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## SYNOPSIS

The graft copolymerization of *N*-vinylpyrrolidone (VP) onto gelatin in aqueous medium, with  $\alpha,\alpha'$ -azobisisobutyronitrile as initiator, has been studied. The effects of various reaction parameters such as temperature, reaction time, as well as the concentrations of initiator, monomer, and gelatin on the percentage of grafting and grafting efficiency were also studied. The chain-transfer constant of isopropanol in this system was calculated. Finally, the grafted samples were analyzed with IR, DSC, TEM, and SEM measurements. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The graft copolymerization of gelatin with vinyl monomer is one of the most effective methods to improve its properties and widen usage. With this method, the graft copolymers not only maintain the special nature of the gelatin itself, but also provide some new properties that gelatin did not have before reaction. Therefore increased attention has been paid to it.

The graft copolymerization of gelatin is generally achieved by free-radical methods, which mainly include  $\gamma$ -radiation initiation and chemical initiation. The latter is more attractive because of convenience. Jesoph et al.<sup>1</sup> grafted butyl acrylate onto gelatin with an H<sub>2</sub>O<sub>2</sub>-ascorbic acid redox system. Misra et al.<sup>2</sup> reported the graft copolymerization of methyl acrylate onto gelatin in aqueous media by using ceric ammonium nitrate as the redox initiator. Kuwajima et al.<sup>3</sup> grafted methyl methacrylate onto gelatin in aqueous solutions using peroxy sulfate,  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN), and benzoyl peroxide as initiator, and found that potassium peroxy sulfate was the most efficient initiator in this particular graft copolymerization. Raghunath and coworkers<sup>4</sup> reported the graft copolymerization of gelatin with *N*-vinylpyrrolidone (VP) by the initiation of

AIBN in a water-isopropanol mixture medium. Previously<sup>5,6</sup> we discussed the graft copolymerization of gelatin with butyl acrylate in aqueous media using ceric ammonium nitrate as initiator, and the use of this graft copolymer in the receiving layer of dye-transfer blank film. Here we discuss the graft copolymerization of VP onto gelatin with AIBN as initiator in aqueous medium.

## EXPERIMENTAL

### Materials

Gelatin (provided by Qing Dao Gelatin Plant) contained 12.7% water. VP (Fluka AG) was packed in Switzerland. AIBN was from the Chemical Company of Tianjin, China.

### Preparation of Graft Copolymer

A known weight of gelatin was slurried in 150 mL distilled water and then poured into a three-neck flask. Under an atmosphere of N<sub>2</sub> and at the appointed temperature, the initiator and monomer were steadily dropped into the vessel. The mixture was allowed to react under slow stirring for several hours. The reacted products were then poured into an excess of acetone, filtered, dried, and weighed.

The weighed products were extracted with trichloromethane in a Soxhlet apparatus for 72 h to

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remove the PVP homopolymer. The extracted products were then dried and weighed.

### Determination of Molecular Weight of Grafted Side Chains

The above dried graft copolymer was refluxed in 6 N HCl (aq.) at 105–110°C for 24 h to hydrolyze the backbone of gelatin into the amino acid, which was removed by dialysis, and the grafted side chains were obtained.

The viscosities of the obtained grafted side chains in aqueous solution were determined at 25°C with a Ubbetohde viscometer, and the weight-average molecular weights were then calculated<sup>7</sup>

$$[\eta] = 6.76 \times 10^{-2} M^{0.55}.$$

### Calculation of Percentage of Grafting (PG) and Grafting Efficiency (GE)

The PG and PE were calculated as follows:

$$PG = \frac{\text{weight of grafted PVP}}{\text{weight of graft copolymer}} \times 100$$

GE

$$= \frac{\text{weight of grafted PVP}}{\text{weight of grafted PVP} + \text{weight of homo-PVP}} \times 100.$$

### IR Spectra

The infrared spectra of gelatin, homo-PVP, and graft copolymer were determined with an FTIR spectrometer.

### Treatment of Grafted Side Chains with Ninhydrin

Approximately 100 mg of the removed grafts were weighed and placed into a test tube containing 2 mL of distilled water. About 2 mL ninhydrin solution was added and thoroughly mixed by gently shaking the tube. The tube was placed in a boiling water bath.

## RESULTS AND DISCUSSION

### Effect of Monomer Concentration

Figure 1 shows the changes of PG, GE, and molecular weight of grafted side chains with monomer

concentration varying. It is evident that with increasing VP, PG and GE both increased and reached a maximum value at a monomer concentration of 0.5 M/L. With a further increase, GE decreased, due to the fact that at higher VP the initiator prefers to initiate monomer rather than gelatin, leading to formation of more homopolymer PVP, thus decreasing GE. The molecular weight of side chains increased continuously as VP increased within the concentrations studied.

### Effect of Initiator Concentration

The effects of initiator concentration on graft copolymerization are illustrated in Figure 2, where both PG and EG first increased with initiator concentration increasing to a concentration of  $6 \times 10^{-3}$  M/L, and then decreasing with AIBN further increasing. The increasing trends of PG and GE may be attributed to the formation of a greater number of graft sites on the gelatin with increasing AIBN. However, beyond the optimum initiator concentration, termination of grafting radicals might occur, decreasing both PG and GE.

### Effect of Gelatin Concentration

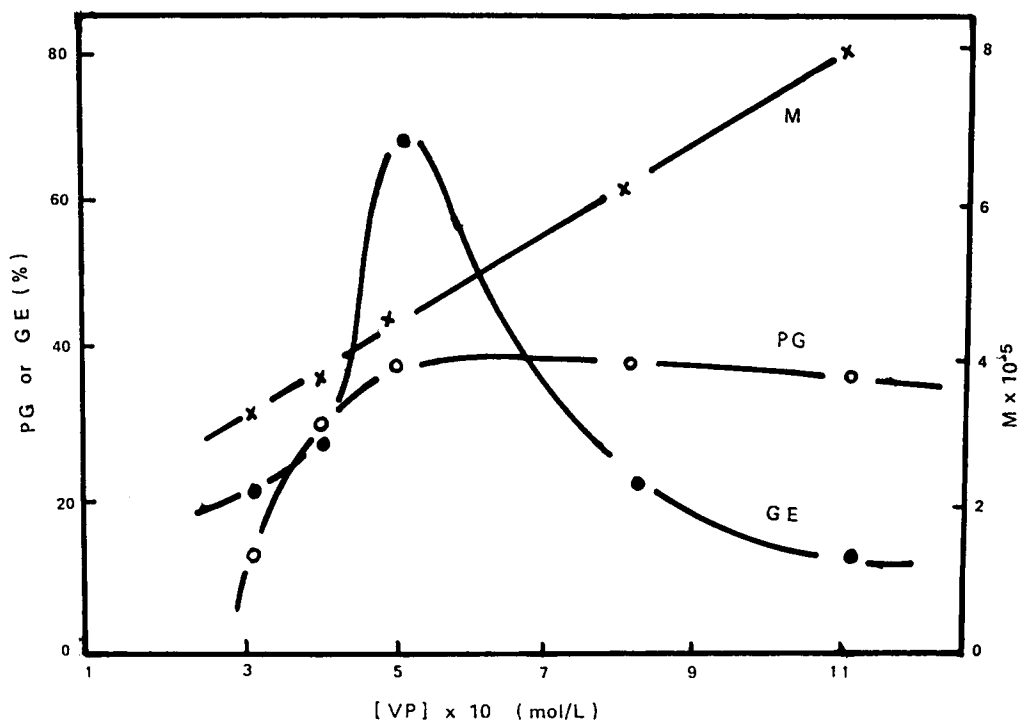
The results in Figure 3 indicated that PG and GE both decreased steadily with gelatin concentration increasing. The gel increase may lead to the following changes:

1. decreasing the ratio of monomer to backbone;
2. increasing the viscosity of the system, thus hindering the rate of graft copolymerization;
3. producing more gelatin macroradicals and increasing the chance of interacting with each other to terminate the graft reaction.

The above three points could explain why PG and GE decreased with gel increasing.

### EFFECT OF TEMPERATURE

The graft copolymerization reaction was studied at five different temperatures ranging from 50 to 80°C (Fig. 4). Raising the temperature favored the diffusion of monomer to polymer backbone and increased the rate of graft copolymerization ( $R_g$ ). Therefore, PG and GE became higher. On the other hand, raising the temperature also increased the rate

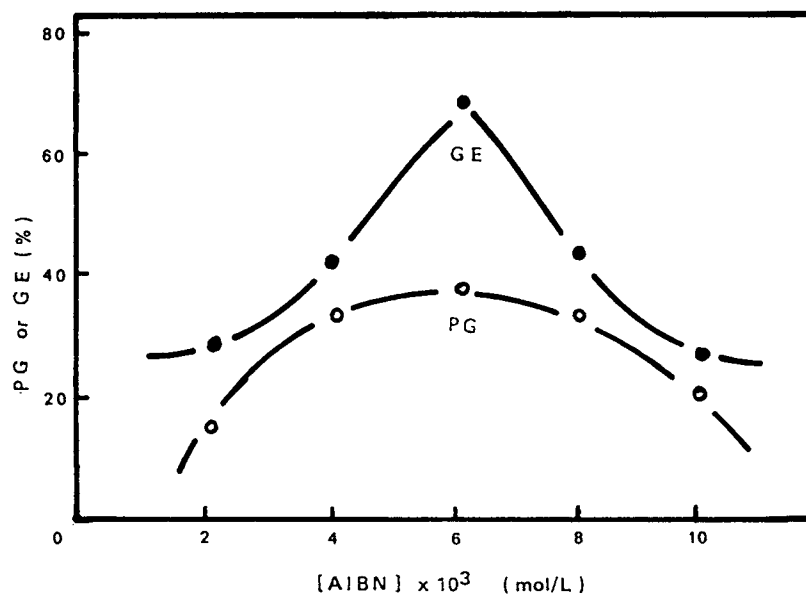


**Figure 1** Effect of VP on grafting. AIBN =  $6 \times 10^{-3}$  M/L, gel =  $2.3 \times 10^{-4}$  M/L, temp. =  $70^{\circ}\text{C}$ , time = 3 h.

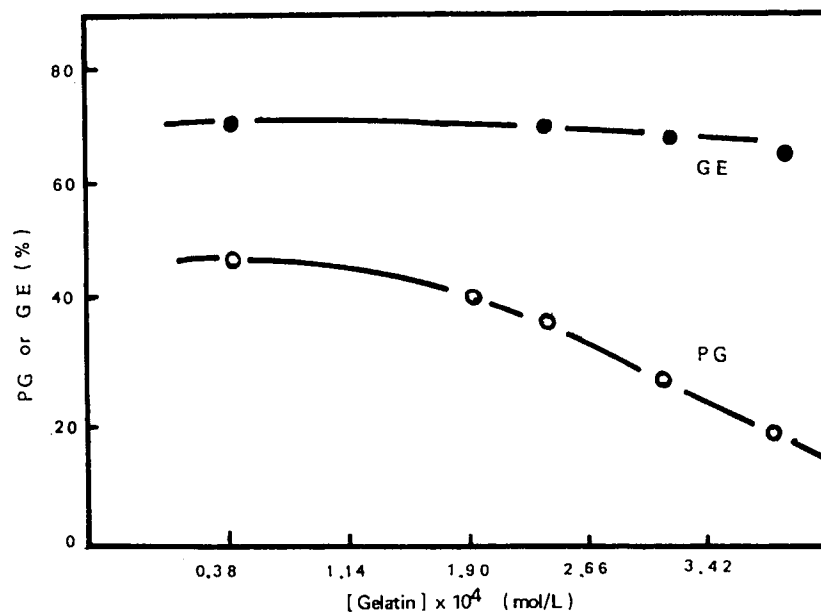
of homopolymerization ( $R_p$ ) of VP, and at higher temperature the increase of  $R_p$  was even faster, leading to decreasing PG and GE. This result is different from the graft copolymerization of gelatin with methacrylate.<sup>8</sup>

#### Effect of Reaction Time

Figure 5 shows the effects of reaction time on graft copolymerization, similar to the result of George et al.<sup>9</sup>



**Figure 2** Effect of AIBN on grafting. VP = 0.5 M/L, gel =  $2.3 \times 10^{-4}$  M/L, temp. =  $70^{\circ}\text{C}$ , time = 3 h.

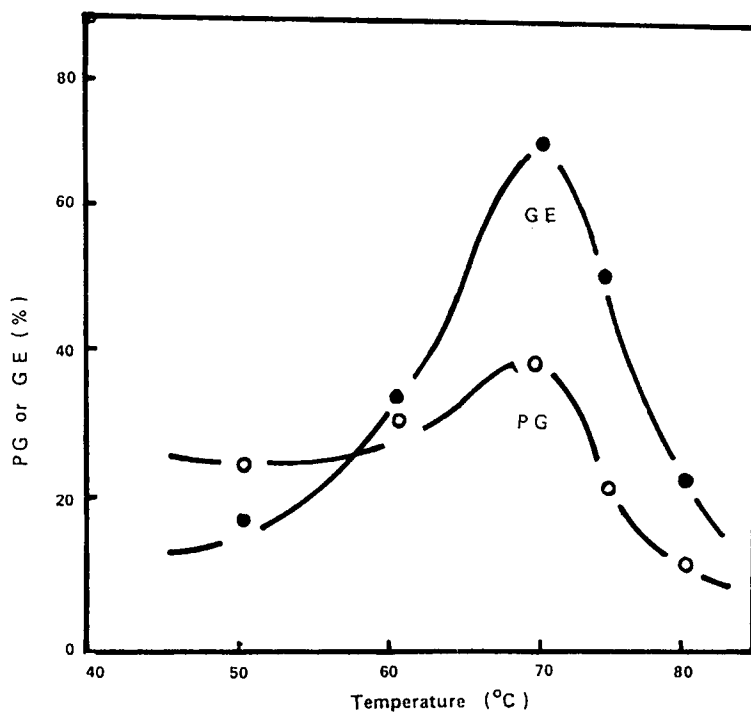


**Figure 3** Effect of gelatin on grafting. VP = 0.5 M/L, AIBN =  $6 \times 10^{-3}$  M/L, temp. = 70°C, time = 3 h.

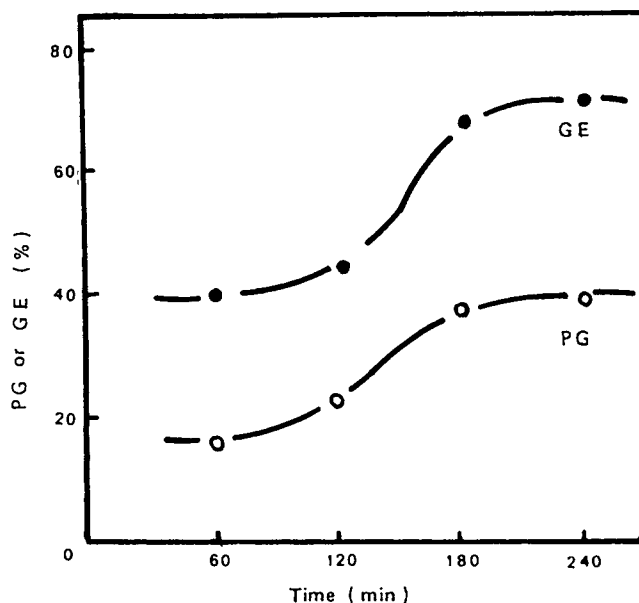
#### Effect of Medium

The graft copolymerizations discussed above were all processed in aqueous medium. Raghunach et al.<sup>4</sup>

reported the same reaction in water-isopropanol (W-I) mixture (1 : 1 v/v). Table I shows the results in these two media. Analyzing the data, the following conclusions can be drawn.



**Figure 4** Effect of temperature on grafting. AIBN =  $6 \times 10^{-3}$  M/L, VP = 0.5 M/L, gel =  $2.3 \times 10^{-4}$  M/L, time = 3 h.



**Figure 5** Effect of reaction time. AIBN =  $6 \times 10^{-3}$  M/L, VP = 0.5 M/L, gel =  $2.3 \times 10^{-4}$  M/L, temp. =  $70^\circ\text{C}$ .

1. PG and GE in the two media were different because of the different solubility of reactants.
2. The changes of PE, GE, and M were the same with initiator concentration changes in the two media.
3. The grafted side chains in the two media were different owing to chain transfers.

The chain-transfer constant,  $C_s$ , of isopropanol was calculated as follows, and the results are listed in Table I. It indicates that the average value of  $C_s$  is  $8.4 \times 10^{-5}$ .

$$\frac{1}{P} = \frac{1}{P_0} + C_s \frac{[S]}{[M]}$$

$$\frac{1}{P} - \frac{1}{P_0} = C_s \frac{[S]}{[M]}$$

$$C_s = \left( \frac{1}{P} - \frac{1}{P_0} \right) \frac{[M]}{[S]}$$

where  $P = 1/M$  and  $P_0 = 1/M_0$ .

### Proof of Grafting

IR spectroscopy has been found to be a valuable method in proving graft copolymerization. Figure 6 shows the IR spectra of gelatin, homo-PVP, and graft copolymer. The spectrum of graft copolymer shows the characteristic absorption of PVP at 1290 and  $1700 \text{ cm}^{-1}$ , in addition to the absorption of gel-

**Table I** Effect of Media

AIBN $\times 10^{-2}$ mol/ $\Delta$	PG (%)		GE (%)		$\bar{M} \times 10^{-4}$		$C_s \times 10^5$
	W-I	W	W-I	W	W-I	W	
2	20.4	14.2	79.9	28.1	9.76	67.7	7.5
4	50.1	33.6	90.5	43.4	8.45	60.5	8.6
6	65.1	38.9	93.1	69.0	7.88	47.6	8.9
8	30.5	34.4	81.4	43.7	7.80	38.8	8.7
10	28.3	21.4	90.1	27.6	6.46	35.7	—

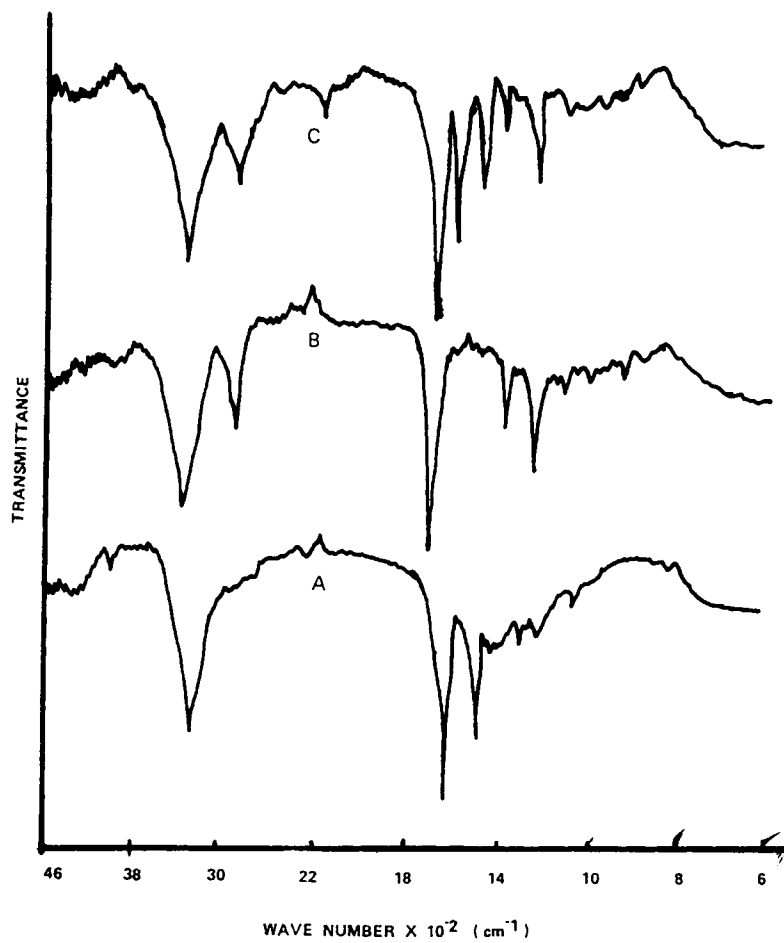
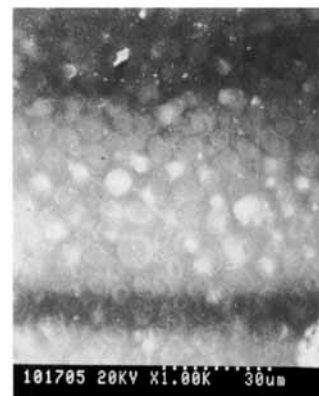
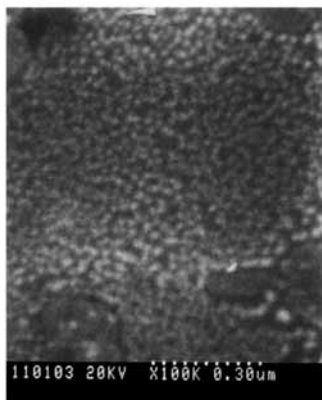
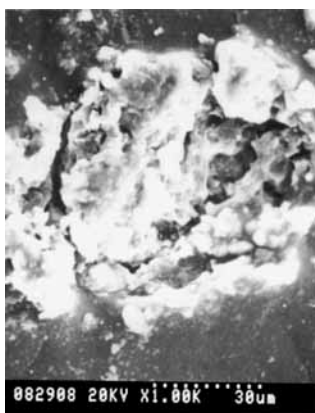


Figure 6 IR spectra: (A) gel, (B) PVP, (C) gel-g-PVP.



(b)

(c)

(a)

Figure 7 SEM photo: (a) Gel-g-PVP ( $\times 1000$ ), (b) Gel-b-PVP ( $\times 1000$ ), (c) Gel-g-PVP ( $\times 100,000$ ).

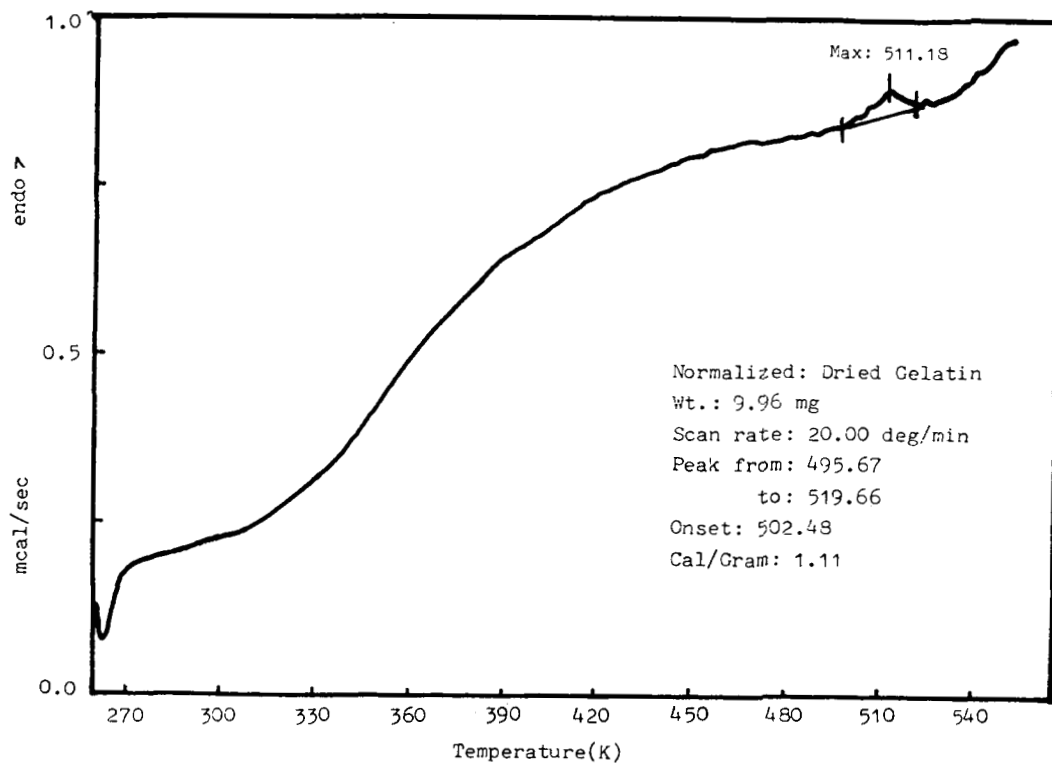


Figure 8 DSC diagram of gelatin.

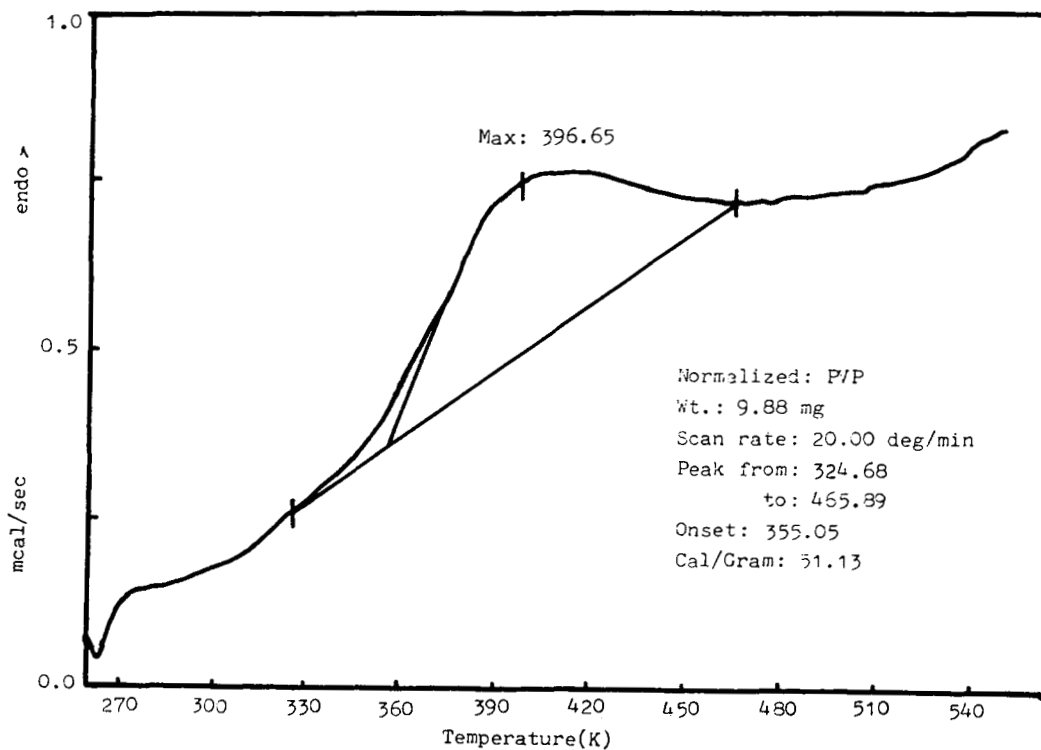


Figure 9 DSC diagram of PVP.

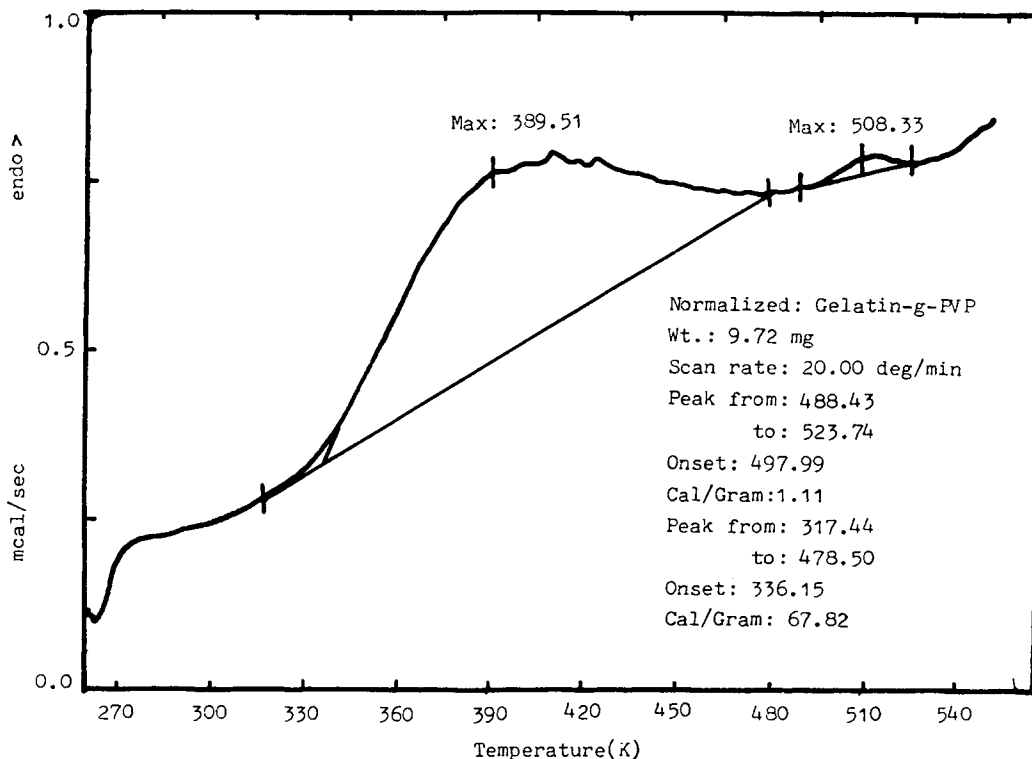


Figure 10 DSC diagram of Gel-g-PVP.

atin at 2550 and 1660  $\text{cm}^{-1}$ . This provides proof for grafting.

Better proof of grafting can be achieved by the detection of amino acid end groups in the grafted side chains isolated by acid hydrolysis of the graft copolymers. The grafted side chains isolated by acid solution from the graft copolymers were treated with ninhydrin reagent, and it was found that the samples gave the characteristic blue color because of the presence of amino acid end groups in grafted side chains. This indicates that actual grafting of the polymer occurred.

#### Microstructure of Graft Copolymer

Figure 7 shows scanning electron micrograph (SEM) photographs of gelatin-*g*-PVP and gelatin-*b*-PVP. The latter is the blend copolymer of gelatin and PVP.

It can be seen, by comparison of Figure 7(a) and (b) that the dispersion of the double phase (gelatin phase and PVP phase) in the graftcopolymer (a) is finer and better than that in the blend copolymer (b). The side chain PVP seems to form microphases attached to the backbone in graft copolymer. (c) is another SEM micrograph of graftcopolymer under higher magnifying power. It also indicates that the

side chain PVP phase dispersed finely among the backbone phase gelatin. The backbone and side chain still existed in separated microphases, which can be demonstrated by differential scanning calorimetry (DSC) analysis. The DSC results are illustrated in Figures 8–10. The glass-transition temperature of dried gelatin is in the range of 496–520°C and for PVP is in the range of 325–466°C. For the graft copolymer gel-*g*-PVP, there are two glass-transition temperatures: 488–523°C, for gelatin, and 317–478°C for PVP. These results indicated that the gelatin backbone and PVP side chain are in separated phases.

#### CONCLUSION

1. AIBN can effectively initiate graft copolymerization of VP onto gelatin.
2. The percentage of grafting, grafting efficiency, and molecular weight of grafted side chain can be adjusted by varying reaction parameters.
3. The graft of VP onto gelatin can proceed in an aqueous, as well as a water-isopropanol medium.



4. The backbone gelatin and grafted side chain PVP exist in separate microphases.

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