Preparation of Gelatin–*N*-Vinylpyrrolidone Graft Copolymer

JIANPING GAO, ZHICHONG LI, WEI WANG, MINGZHI HUANG

Department of Chemistry, Tianjin University, Tianjin 300072, People's Republic of China

ABSTRACT: The graft copolymerization of *N*-vinylpyrrolidone (VP) onto gelatin was carried out by the following four different initiator systems: AIBN, $K_2S_2O_8$, H_2O_2—Fe^{2+}, and Ce^{4+}—HNO_3. The last one caused the monomer to lose the double-bond and polymerization ability due to the hydrolysis of the monomer. Using α,α-azobisisobutyronitrile as an initiator, the graft copolymerization of gelatin and *N*-vinyl-pyrrolidone in aqueous medium was studied systematically. The relationships between the rate of grafting and the concentration of initiator, monomer, and gelatin were established experimentally. Meanwhile, the rate equation was also derived from the proposed reaction mechanism, and it was similar to the equation previously obtained experimentally. The apparent activation energies for homopolymerization (E_h), graft copolymerization (E_g), and over all polymerization (E_p) were calculated. The graft efficiency and molecular weight of the grafted PVP were measured by hydrolyzing the backbone with hydrochloric acid. The graft copolymers Gel-*g*-PVP were added into the coating films, and the physical properties of the films, such as hardening ability, dimensional stability, and wetting property were investigated. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1485–1492, 1998

Key words: gelatin; *N*-vinylpyrrolidone; graft copolymerization; graft mechanism

INTRODUCTION

The graft copolymerization of gelatin with various vinyl monomers is an effective method to improve the properties of the gelatin. Croome has reviewed the application of graft copolymers in photographic materials. It is said that the addition of graft copolymers can improve the strength and heat resistance of the light-sensitive film and decrease its sensitivity to low humidity in surrounding medium.[1]

The graft copolymerization of gelatin can be prepared by different initiating systems.[2–5] Joseph has compared the graft copolymerization of methyl methacrylate (MMA) with gelatin using two different initiators.[6,7] In our previous articles, we discussed the graft copolymerization of butyl acrylate onto gelatin[8] and described the application of the graft copolymer Gel-*g*-PBA in the dye-transferring blank film.[9] We also studied the graft copolymerization of *N*-vinylpyrrolidone (VP) onto gelatin and MMA onto starch.[10,11] As an extension, the present article discusses the mechanism of the graft copolymerization of gelatin with *N*-vinylpyrrolidone and the application of the graft copolymers in the coating film.

EXPERIMENTAL

Materials

Gelatin was provided by Qingdao Gelatin Plant. *N*-vinylpyrrolidone, Fluke AG, was packaged in

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Switzerland. AIBN (α,α-azobisisobutyronitrile) came from Chemical Company of Tianjin, Tianjin, P. R. China.

Manufacture of Graft Copolymer

A known amount of gelatin was slurred in 150-mL distilled water and then poured into a three-neck flask. Under an atmosphere of N_2 gas and at the appointed temperature, the initiator and monomer were dropped into the vessel. The content was allowed to react under stirring for several hours. The products were then poured into excess of acetone to precipitate, then filtered, dried, and weighed.

The rough products were extracted with trichloromethane in a Soxhlet apparatus for 72 h to remove the homopolymer PVP from the graft copolymer. The refined products were then dried and weighed again.

Hydrolysis of the Graft Copolymer

The above refined graft copolymer was refluxed in $6N$ HCl (aq.) at $105-110°C$ for 24 h to hydrolyze the backbone of gelatin into amino acids, which were removed by dialysis.

Determination of Molecular Weight of PVP Grafted

The intrinsic viscosity of the grafted PVP aqueous was measured at 25°C with a Ubbelodhe viscometer, and the molecular weight of PVP was calculated by the Mark–Houwink equation,[12] as follows:

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

Calculation of Percentage of Grafting (*PG*) and Graft Efficiency (*GE*)

The percentage of grafting (*PG*) and graft efficiency (*GE*) were calculated as follows:

$$PG\ (\%) = \frac{\text{Weight of grafted PVP}}{\text{Weight of graft copolymer}} \times 100$$

$$GE\ (\%) = \frac{\text{Weight of grafted PVP}}{\begin{array}{c}\text{Weight of grafted PVP}\\ +\ \text{weight of homo-PVP}\end{array}} \times 100$$

Preparation of the Film Sample

The coating film was prepared by adding the graft copolymer into the ordinary coating formulation,

casting the mixture into a film, and drying it over 30 days before test.

Measurement of Dimensional Stability

The prepared film was soaked in distilled water at 40°C for 24 h, and then the length (L) of the film under wetting condition was measured. The percentage of the expansion of the film (ε) was calculated as follows:

$$\varepsilon = \frac{L - L_0}{L_0} \times 100$$

where L_0 is the original length of the sample before soaking.

Determination of Hardening Ability

The film dried over a month was weighed W_0 and dipped into 40°C distilled water for 24 h. Then it was taken out and dried in air to a constant weight, W. The lost percentage that represents the hardening ability of the film (β) was calculated as follows:

$$\beta = \frac{W_0 - W}{W_0} \times 100$$

Measurement of Wetting Properties

The wetting angle θ_{H_2O} of the film was measured on a contact angle measuring apparatus using water as the wetting agent.

RESULTS AND DISCUSSION

The Effect of Initiators on the Grafting

We selected four initiator systems to determine their initiating ability in the graft copolymerization of VP onto gelatin. They are α,α-azobisisobutyronitrile (AIBN), potassium persulfate ($K_2S_2O_8$), peroxide–ferrous ($H_2O_2-Fe^{2+}$), and $Ce^{4+}-HNO_3$. But experimental results proved that $Ce^{4+}-HNO_3$ was not suitable to be used in this system because HNO_3 could cause the monomer VP to hydrolyze and lose the double bonds. As for peroxider–ferrous and potassium persulfate, they also caused the hydrolysis of the VP to some extent when gelatin was absent, but they did initiate the copolymerization of VP in the presence of gelatin, which
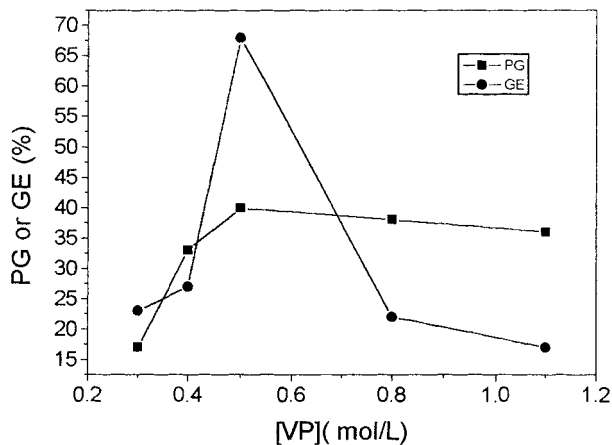
Figure 1 Effect of [VP] on grafting with AIBN as an initiator: [AIBN] = 6 × 10^{-3} mol/L; [Gel] = 2.3 × 10^{-4} mol/L; temperature = 70°C; time = 3 h.

Figure 3 Effect of [VP] on grafting with H_2O_2—Fe^{2+} as an initiator: [H_2O_2] = 6 × 10^{-3} mol/L; [Fe^{2+}] = 2 × 10^{-3} mol/L; [Gel] = 2.3 × 10^{-4} mol/L; temperature = 70°C; time = 3 h.

suggested that perhaps gelatin acted as buffer to reduce the hydrolysis of VP.

Figure 1 shows the effect of VP concentration on the *PG* and *GE* using AIBN as an initiator. As the [VP] increased, *PG* increased steadily and approached a constant, while *GE* rose first to a maximum and then fell. The decrease of *GE* is due to the increasing homopolymerization of VP as a competitive reaction. Figure 2 shows the effect of temperature on the graft copolymerization under the same initiator. Both *PG* and *GE* increased first and then decreased when the reaction temperature rose, which is true of other graft copolymerization of monomers onto gelatin.[8]
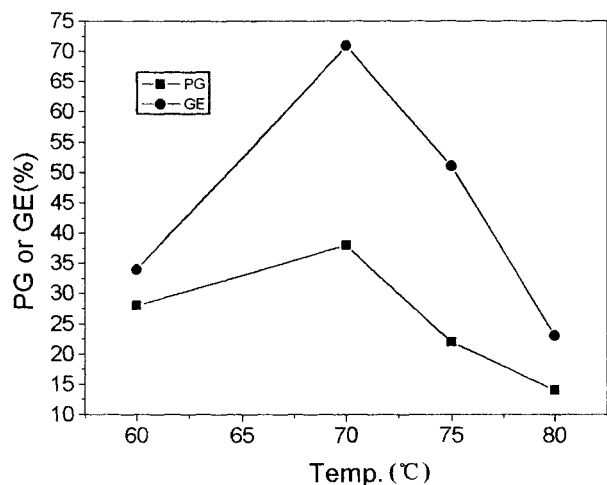
Figures 3 and 4 show the effect of VP concentration and reaction temperature on grafting under the initiating of H_2O_2–Fe^{2+}. Unlike the changes of *PG* and *GE* in AIBN, *PG* and *GE* both grew with the increase of [VP]. Since part of the monomers, in the presence of H_2O_2–Fe^{2+}, suffered hydrolysis, higher [VP] offers a higher effective [VP]. *PG* and *GE* both dropped as the temperature went up, which was different from that of AIBN, which showed a maximum value. In fact, H_2O_2–Fe^{2+} also exhibits maximum values, but they shift to lower temperature because of the lower decomposition energy of the redox system.

Figure 2 Effect of temperature on grafting with AIBN as an initiator: [AIBN] = 6 × 10^{-3} mol/L; [Gel] = 2.3 × 10^{-4} mol/L; [VP] = 0.5 mol/L; time = 3 h.
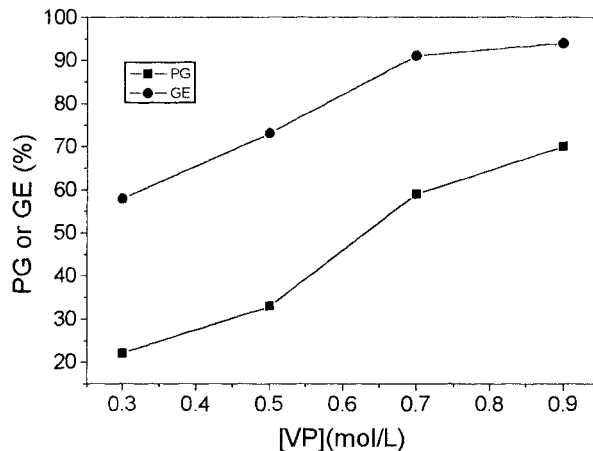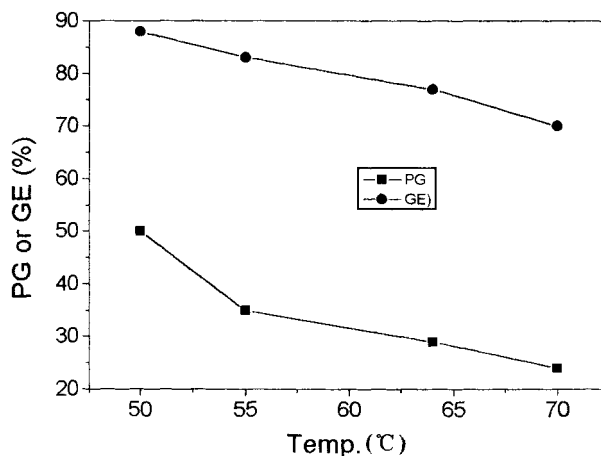

Figure 4 Effect of temperature on grafting with H_2O_2—Fe^{2+} as an initiator: [H_2O_2] = 6 × 10^{-3} mol/L; [Fe^{2+}] = 2 × 10^{-3} mol/L; [Gel] = 2.3 × 10^{-4} mol/L; [VP] = 0.5 mol/L; time = 3 h.
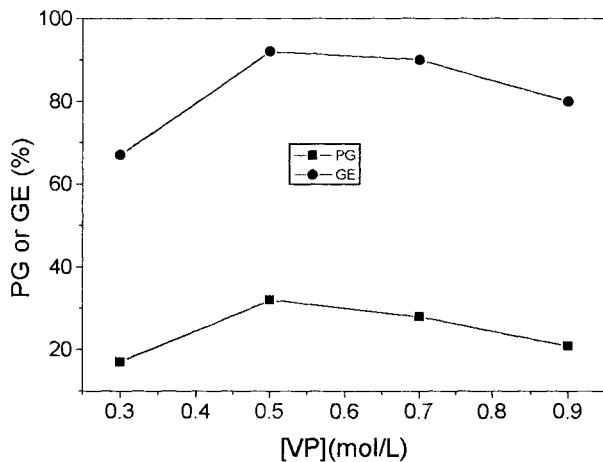
Figure 5 Effect of [VP] on grafting with $K_2S_2O_8$ as an initiator: $[K_2S_2O_8] = 6 \times 10^{-3}$ mol/L; [Gel] = 2.3 $\times 10^{-4}$ mol/L; temperature = 70°C; time = 3 h.

Figure 7 Plot of R_g versus $[AIBN]^{0.5}$: [Gel] = 2.3×10^{-4} mol/L; [VP] = 0.5 mol/L; temperature = 70°C; time = 3 h.

Figures 5 and 6 show the initiating ability of $K_2S_2O_8$. When temperature increased the response of *PG* was similar to that of AIBN, but the response of *GE* was similar to that of the redox system $H_2O_2 - Fe^{2+}$.

Rate of Grafting (R_g)

The graft process of *N*-vinylpyrrolidone onto gelatin, using AIBN as an initiator, contains a pair of competitive reactions. One is the graft copolymerization of VP onto gelatin, and the other is the homopolymerization of VP. The two o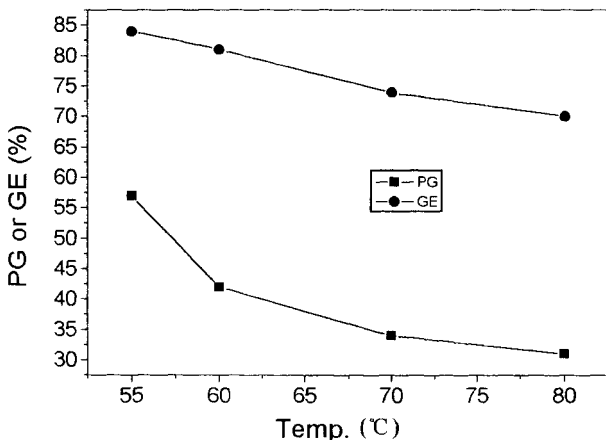pposite reaction rates are all dependent on the reaction temperature and concentration of the initiator, monomer, and gelatin.

The relationship between initiator concentration and the rate of grafting is shown in Figure 7. It indicates that the R_g increased with increasing [AIBN] and depended on one-half power of [AIBN].

Figure 8 shows the effect of gelatin concentration on the R_g. Similarly, R_g is directly proportional to $[Gel]^{1/2}$.

The effect of monomer concentration on the rate of grafting is illustrated in Figure 9. It suggested that the plot of R_g versus [VP] is linear.

According to the above results, the following equation can be established:

Figure 6 Effect of temperature on grafting with $K_2S_2O_8$ as an initiator: $[K_2S_2O_8] = 6 \times 10^{-3}$ mol/L; [Gel] = 2.3×10^{-4} mol/L; [VP] = 0.5 mol/L; time = 3 h.
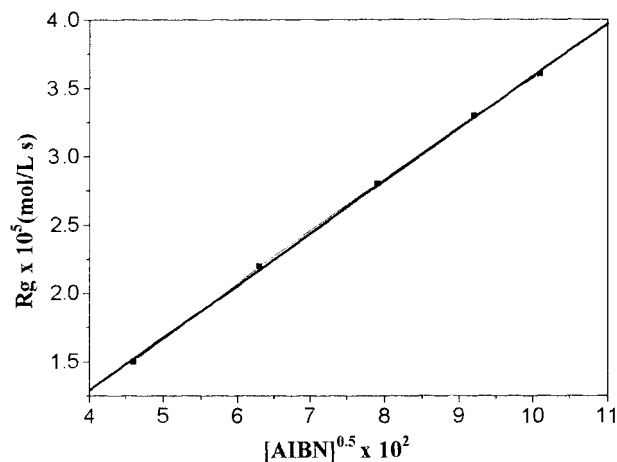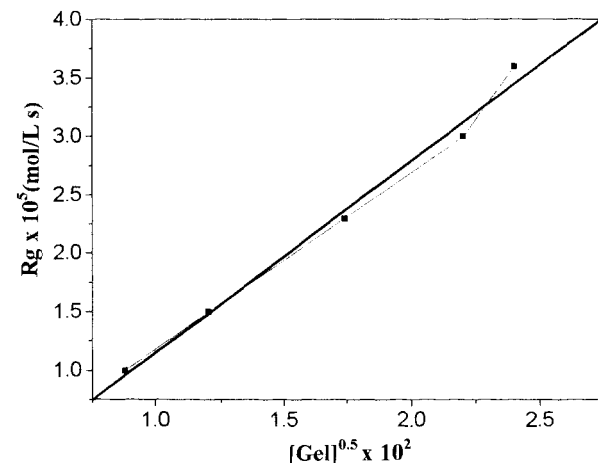

Figure 8 Plot of R_g versus $[Gel]^{0.5}$: [AIBN] = 6×10^{-3} mol/L; [VP] = 0.5 mol/L; temperature = 70°C; time = 3 h.
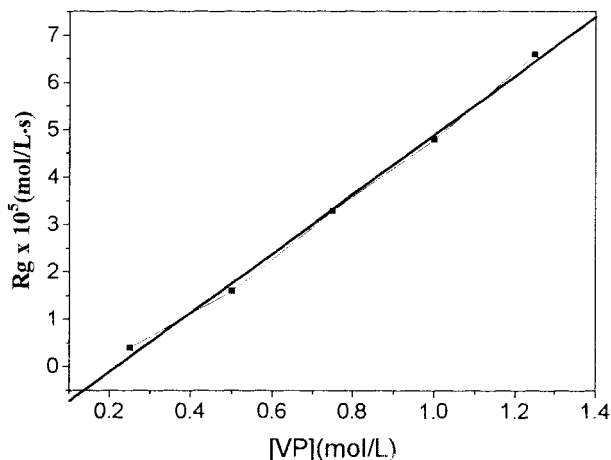
Figure 9 Plot of R_g versus [VP]: [AIBN] = 6×10^{-3} mol/L; [Gel] = 2.3×10^{-4} mol/L; temperature = 70°C; time = 3 h.

$$R_g = K[\text{AIBN}]^{1/2}[\text{VP}][\text{Gel}]^{1/2} \qquad (1)$$

Besides, the effect of the temperature on the rate of homopolymerization of VP(R_h), graft copolymerization of VP onto gelatin(R_g), and total polymerization (R_p) was studied within the range of 60–80°C, and the results are shown in Figures 10 and 11. From the slopes of the plots, the apparent activation energies for graft copolymerization (E_g), homo-polymerization (E_h), and over all polymerization (E_p) were calculated, where $E_g = 23.2$ kj/mol, $E_h = 45.5$ kj/mol, and $E_p = 25.5$ kj/mol.

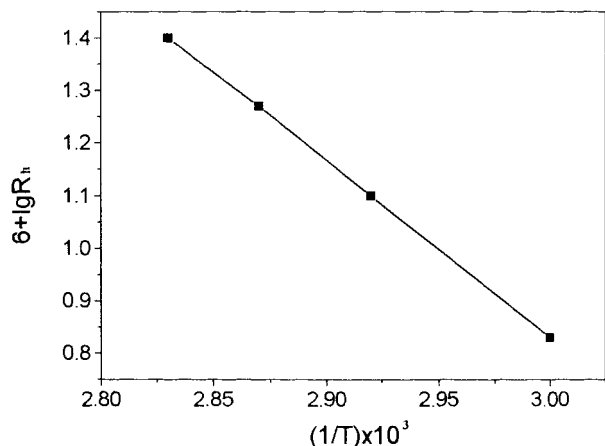Evidently, the energy for graft copolymerization is almost half of that for the homopolymeriza-

Figure 10 Plot of $\lg R_h$ versus $1/T$: [AIBN] = 6×10^{-3} mol/L; [Gel] = 2.3×10^{-4} mol/L; [VP] = 0.5 mol/L; time = 3 h.
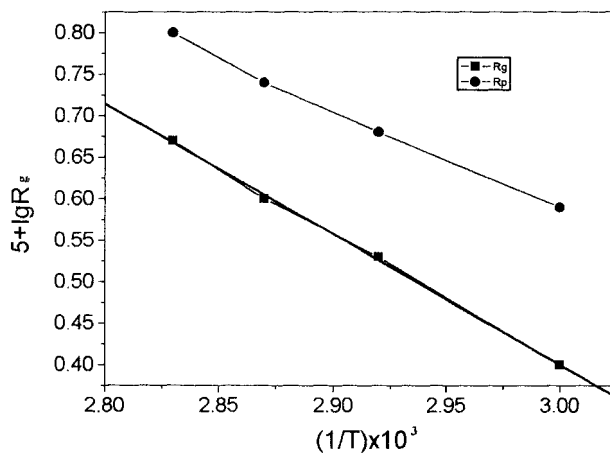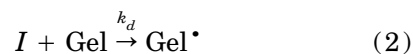

Figure 11 Plot of $\lg R_g$ or $\lg R_p$ versus $1/T$: [AIBN] = 6×10^{-3} mol/L; [Gel] = 2.3×10^{-4} mol/L; [VP] = 0.5 mol/L; time = 3 h.

tion, which indicates that the initiating rate of radical on the backbone of gelatin is larger than that on the monomers.

Reaction Mechanism

The mechanism of this specific graft copolymerization is expected to proceed as in the following scheme.

Initiation

$$I + \text{Gel} \xrightarrow{k_d} \text{Gel}^\bullet \qquad (2)$$

$$\text{Gel}^\bullet + M \xrightarrow{k_i'} \text{Gel}M^\bullet \qquad (3)$$

$$I + M \xrightarrow{k_i} M^\bullet \qquad (4)$$

Propagation

$$\text{Gel}M^\bullet + nM \xrightarrow{k_p^1} \text{Gel}M_nM^\bullet \qquad (5)$$

$$M^\bullet + nM \xrightarrow{k_p^2} M_nM^\bullet \qquad (6)$$

Termination

$$\text{Gel}M_x^\bullet + \text{Gel}M_y^\bullet \xrightarrow{k_t^1} \text{graft copolymer} \qquad (7)$$

$$\text{Gel}M_n^\bullet + M_m^\bullet \xrightarrow{k_t^2} \text{graft copolymer} \qquad (8)$$

$$M_n^\bullet + M_m^\bullet \xrightarrow{k_t^3} \text{homopolymer} \qquad (9)$$
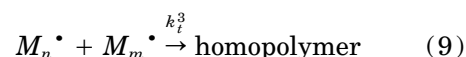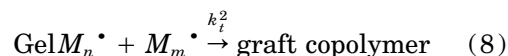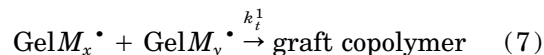
where M, I, and gel represent the monomer, initiator, and gelatin, respectively. It is assumed that $k_p^1 = k_p^2 = k_p$ because the reactive propagation centers are the same, no matter which polymerization it is, homopolymerization or graft copolymerization. This is confirmed by the molecular weight to be discussed later. Under the same reaction conditions, the molecular weight of the homopolymer PVP is in the same order as that of the grafted PVP onto gelatin as branches, and the monomer is mainly consumed in the course of propagation. Similarly, it is also supposed that $k_t^1 = k_t^2 = k_t^3 = k_t$ due to the following reasons.

1. The three termination reactions are under the same reaction conditions.
2. The reaction centers are the same, with only the length of the chains being different.
3. The molecular weight of the PVP grafted or homopolymer PVP is high enough, so that the effect of gelatin can be neglected if only the length of the chain is concerned.
4. The backbones of the gelatin and PVP are both water-soluble polymers, so the existence of gelatin does not bring about a gel effect.

Now applying the three basic hypotheses to free radical polymerization, the equation for the graft copolymerization can be derived as follows.

$$d[M^\bullet]/dt = k_i[I][M]$$
$$- k_t[M^\bullet]^2 - k_t[Gel^\bullet][M^\bullet] = 0 \quad (10)$$

$$ki[I][M] = k_t[M^\bullet]^2 + k_t[Gel^\bullet][M^\bullet] \quad (11)$$

$$d[Gel^\bullet]/d_t = k_d[I][Gel] - k_t[GelM^\bullet]^2$$
$$- k_t[Gel^\bullet][M^\bullet] = 0 \quad (12)$$

$$k_d[I][Gel] = k_t[GelM^\bullet]^2 + k_t[Gel^\bullet][M^\bullet] \quad (13)$$

$$[GelM^\bullet] = \frac{k_d[I]^{1/2}[Gel]}{k_t^{1/2}(k_i[M] + k_d[Gel])^{1/2}} \quad (14)$$

$$R_g = k_p[Gel^\bullet][M]$$
$$= k_p \frac{k_d[I]^{1/2}[Gel][M]}{k_t^{1/2}(k_i[M] + k_d[Gel])^{1/2}} \quad (15)$$

In the previous part of this article, we have discussed the apparent activation energy for graft copolymerization (E_g) and homopolymerization (E_h). This indicates that the initiating rate of the graft copolymerization is larger than that of the homopolymerization. Therefore, $k_d[Gel] \gg k_i[M]$

is suitable, and the denominator can be simplified as follows:

$$(k_i[M] + k_d[Gel])^{1/2} \approx k_d[Gel]^{1/2} \quad (16)$$

Thus,

$$R_g = \frac{k_p k_d^{1/2}}{k_t^{1/2}}[I]^{1/2}[M][Gel]^{1/2} \quad (17)$$

$$R_g = K[I]^{1/2}[M][Gel]^{1/2} \quad (18)$$

where

$$K = \frac{k_p k_d^{1/2}}{k_t^{1/2}}$$

Equation (18) is identical with eq. (1), established from experimental results.

Molecular Weight of the Grafted Side Chains

The change of the molecular weight of the grafted PVP with the variation of reaction conditions is discussed. The molecular weight was measured by the viscosity method, and the results are listed in Table I. It can be seen that the molecular weights of the grafted chains are within the range of 2.43×10^5 to 8.01×10^5. Increasing the monomer concentration could increase the molecular weight, but increasing [AIBN] was just the opposite. The effect of reaction temperature is complex; the molecular weight rose with the increase of reaction temperature and reached a maximum value of 4.76×10^5 at temperature of 70°C.

Except for the molecular weight of the grafted side chain, the molecular weight of the homopolymer of PVP produced during the graft copolymerization was also measured, and the values are listed at the bottom of Table I. The data show that the molecular weight of the grafted chain was greater than that of homopolymer PVP, and the difference was even outstanding at the higher initiator concentration. The difference could be attributed to the following reasons.

1. The formation of the radical on the backbone is easier than that of the monomer for homopolymerization, so the grafted side chain is longer than that of the homopolymer PVP under the same reaction conditions and it becomes more and more evident with the increasing initiator concentration.

Table I   Molecular Weights of Grafted Side Chains

Factors		$M \times 10^{-5}$	Other Conditions
[VP] $\times$ 10 mol/L	3	3.13	[AIBN] = 6×10^{-3} mol/L
	4	3.86	[Gel] = 2.3×10^{-4} mol/L
	5	4.76	Temp = 70°C
	8	6.07	Reaction time = 3 h
	11	8.01	
Temperature (°C)	50	1.35	[AIBN] = 6×10^{-3} mol/L
	60	2.53	[Gel] = 2.3×10^{-4} mol/L
	70	4.76	[VP] = 0.5 mol/L
	75	3.65	Reaction time = 3 h
	80	2.46	
[AINB] $\times$ 10^3 mol/L	2	6.77	[VP] = 0.5 mol/L
	4	6.05	[Gel] = 2.3×10^{-4} mol/L
	6	4.76	Temp = 70°C
	8	3.88	Reaction time = 3 h
	10	3.57	
[AINB] $\times$ 10^3 mol/L	2	4.68	[VP] = 0.5 mol/L
	4	3.75	[Gel] = 2.3×10^{-4} mol/L
	6	2.94	Temp = 70°C
	8	2.18	Reaction time = 3 h
	10	1.27	

2. The termination of the macroradicals connected to the gelatin may be slightly hindered by the long-chain backbone.

Properties of the Film Added with Copolymers Gel-*g*-VP

The properties such as transparency, prewetting property (θ_{H_2O}), dimensional stability (ϵ), and hardening ability (β) of the film added with Gel-*g*-VP were determined, and the data are listed in Table II. It can be seen that addition of graft copolymer Gel-*g*-VP did not bring about any detrimental effects on the transparency and dimensional stability of the film. Meanwhile, the surface wetting angle evidently decreased by adding Gel-*g*-VP. This means an increase in prewetting behavior of the film, which is favorable for the improvement of the dye-transferring property.

CONCLUSION

1. The apparent activation energies are $E_g = 23.2$ kj/mol, $E_h = 45.5$ kj/mol, and $E_p = 25.5$ kj/mol.
2. The rate of the graft copolymerization of VP onto gelatin is

$$R_g = K[I]^{1/2}[M][\text{Gel}]^{1/2}.$$

3. The molecular weight of the grafted PVP is greater than that of homopolymer PVP.
4. Adding graft copolymer Gel-*g*-VP can improve the prewetting ability of the film.

Table II   Some Properties of the Film

Samples	Amount Added (wt %)	Wetting Angle θ_{H_2O} (°)	Transparency (%) λ = 600 nm	ϵ	β
I	0	87	88.7	31.4	0.370
II[a]	10	69	89.8	31.7	0.377
III[b]	10	72	90.1	30.1	0.506

[a] II: Gel-*g*-VP, PVP/Gelatin = 20/100.
[b] III: Gel-*g*-VP, PVP/Gelatin = 40/100.

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