Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Graft Copolymerization of Butyl Acrylate onto Gelatin in the Presence of Ceric Ion

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To cite this Article Li, Zhi-Chong , Fu, Zhi-Fong , Huang, Ming-Zhi and Lian, Na(1988) 'Graft Copolymerization of Butyl Acrylate onto Gelatin in the Presence of Ceric Ion', Journal of Macromolecular Science, Part A, 25: 12, 1487 — 1513
To link to this Article: DOI: 10.1080/10601328808055084
URL: http://dx.doi.org/10.1080/10601328808055084

J. MACROMOL. SCI.—CHEM., A25(12), pp. 1487-1513 (1988)

GRAFT COPOLYMERIZATION OF BUTYL ACRYLATE ONTO GELATIN IN THE PRESENCE OF CERIC ION

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ABSTRACT

The graft copolymerization of butyl acrylate (BA) onto gelatin with ceric ammonium nitrate (CAN) as redox initiator in an aqueous medium has been studied. The products were characterized by IR. The effects of various reaction parameters, including reaction time and temperature, concentrations of gelatin, monomer, initiator, and nitric acid, on the percentage of grafting, the grafting efficiency, and the rate of graft copolymerization were studied systematically. The influences of some inorganic salts, organic additives, and the emulsifier were also investigated. The disappearing rate of Ce(IV) during the period of reaction was observed. The activation energy of graft copolymerization, homopolymerization, and total polymerization were calculated. The reaction mechanism is discussed, and rate equations of the reaction are proposed.

INTRODUCTION

In recent years, more and more attention has been devoted to the study of graft copolymerization onto gelatin and the resulting products. Much work has been reported in this field [1]. Through the graft copolymerization, various polymeric chains can be introduced onto gelatin macromolecules, and the modified gelatin will have some new useful properties, thus extending their use in different fields.

From published work it can be concluded that most of the grafting reactions were carried out in aqueous medium, or sometimes in water-acetic acid [2] or in water-isopropanol [3]. The initiators used were mostly persulfates [4], azo compounds [5], organic peroxides [6], or hydrogen peroxide-ascorbic acid [7]. Ceric salts were used more recently [8-10]. The monomers used for grafting can be divided into two groups–hydrophilic and hydrophobic, the former involving acrylic acid, methacrylic acid, acrylamide, vinylpyridine, and vinylpyrrolidone, the latter acrylonitrile, acrylates, methacrylates, styrene, etc.

Poly(butyl acrylate) has a low glass-transition temperature and quite good elasticity. Grafting it onto gelatin can greatly improve its physicomechanical properties, especially by increasing the strength of the gelatin film, which is very important for light-sensitive materials.

Ceric salts have been extensively used as redox initiators in graft copolymerization of vinyl monomers onto wool [11], cellulose [12], collagen [13], etc. As gelatin molecules have many reactive groups, like hydroxyl, amino, imino, mercapto, etc., the ceric ion can initiate the grafting reaction on it. In addition, the ceric ion-initiated system will have no deleterious effect on the photographic emulsion characteristics.

We are interested in grafting butyl acrylate onto gelatin. In this paper the graft copolymerization was carried out in water with Ce(IV) as a redox initiator. The reaction parameters have been studied, and the reaction mechanism is proposed. The details of product analysis and the use in the receiving layer of dye-transfer blank film will be reported in a later paper.

EXPERIMENTAL

Materials

The gelatin used was an inert one of photographic grade, water content 13.3%, produced by Qingdao Gelatin Manufactory.

Butyl acrylate (BA), chemically pure, was first washed with 5% sodium hydroxide to remove the inhibitor, then washed with water to remove the

alkali, and finally dried over anhydrous calcium chloride. Purification was effected by distillation under vacuum, and the middle fraction was collected and used.

Ceric ammonium nitrate (CAN), analytical grade, was used as received. All other chemicals were reagent grade.

Preparation of Graft Copolymers

The graft reactions were carried out in a three-necked round-bottom flask of 250 mL (or 100 mL) capacity, fitted with a water-sealed glass-stirrer, a N_2 gas inlet, and a reflux condenser. The reaction temperature was controlled to an accuracy of ±1°C in a constant-temperature water bath.

In a typical experiment a weighed amount of gelatin was first swelled with distilled water, then heated and dissolved to obtain an aqueous solution of the required concentration. This was poured into the reaction flask, stirred, and bubbled with N_2 gas for 1 h. The required amount of BA was added, followed by the desired amount of CAN dissolved in a definite volume of nitric acid. The reaction proceeded at a fixed temperature under N_2. After the desired period of time, some ammonium ferrous sulfate was added to stop the reaction. Then the ingredients were poured into cold acetone, and the grafted gelatin was precipitated. The products were filtered and dried under vacuum.

The dried products were Soxhlet extracted with acetone for 72 h to remove the homopolymer poly(butyl acrylate) (PBA) thoroughly. The purified graft copolymer was also dried under vacuum and weighed.

Determination of the Percentage of Grafting, Grafting Efficiency, and the Rate of Graft Copolymerization

The percentage of grafting (G), the grafting efficiency (E), and the rate of graft copolymerization R_g, as well as the rates of homopolymerization (R_h) and total polymerization (R_p), can be calculated by weighing the original gelatin and grafting products:

$$G = \frac{\text{weight of grafted product} - \text{weight of gelatin}}{\text{weight of gelatin}} \times 100$$

$$= \frac{\text{weight of grafted PBA}}{\text{weight of gelatin}} \times 100.$$

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

$$R_g = \frac{\text{weight of grafted PBA}}{\text{MW of BA} \times \text{reaction time (s)} \times \text{reaction volume (mL)}} \times 1000.$$

$$R_h = \frac{\text{weight of homo-PBA}}{\text{MW of BA} \times \text{reaction time (s)} \times \text{reaction volume (mL)}} \times 1000.$$

$$R_p = R_g + R_h.$$

The above characteristics can also be evaluated by the nitrogen contents of the materials, determined by Kjeldahl's method, e.g.,

$$G = \frac{N - N'}{N'} \times 100,$$

where N and N' represent the nitrogen content of the gelatin and the graft copolymer, respectively.

A comparison of the results of the above two methods indicated that they were nearly identical.

Measurement of the Disappearing Rate of Ceric Ion [14]

After a given period of reaction time, an excess amount of ammonium ferrous sulfate solution was added to the reaction system, then back titrated with ceric ammonium sulfate standard solution in the presence of Ferroin indicator. Thus the rate of disappearance of Ce(IV) (R_c) could be calculated.

IR Spectra

The infrared spectra of gelatin, homo-PBA, and graft copolymer were determined with a FT-IR spectrometer.

RESULTS AND DISCUSSION

Evidence of Grafting

Solvent Extraction. The simplest method to prove the formation of graft copolymer is based on differences in solubility between the graft copolymer

and the nongrafted loosely bound homopolymer. Gelatin is soluble in hot water, and homo-PBA in acetone. When a reaction product was Soxhlet extracted with acetone and hot water alternatively for a long time, insoluble solid still remained. A physical mixture of gelatin and homo-PBA treated in the same way was found to dissolve completely. Therefore, it is apparent that the grafting product obtained was not a simple physical mixture, but some chemical bonds must exist between gelatin and PBA macromolecules.

IR Spectra. The formation of graft copolymer was further confirmed by IR spectroscopy. The IR spectra of pure gelatin, homo-PBA, and the graft copolymer are shown in Fig. 1. In the IR spectrum of pure gelatin (Fig. 1A), the strong characteristic bands of the amide groups at 1660 and 1550 cm^{-1} can be observed. Figure 1(B), the IR spectrum of homo–PBA, shows carbonyl-group absorption at 1730 cm^{-1}. Figure 1(C), the IR spectrum of graft copolymer, shows both the amide peaks (1660, 1550 cm^{-1}) and the carbonyl peak (1730 cm^{-1}). As the graft copolymer had been purified by thorough extraction with acetone and hot water, it was free from homo-PBA and pure gelatin. Therefore, the formation of graft copolymer was confirmed by the IR spectra.

Percentage of Grafting and Grafting Efficiency

Effect of Time. As shown in Fig. 2, the percentage of grafting (G) increased with reaction time, but the grafting efficiency (E) was almost unchanged. This is explained by the fact that the longer the reaction time, the more sites on the gelatin macromolecules are activated by ceric ion, followed by more grafting, which increases G, while E was unaffected by time. This result is similar to the grafting of vinyl monomers onto cellulose with ceric ion as an initiator [15], but is different from Misra's work [8, 9], which reported that in the Ce(IV)-initiated graft copolymerization of methyl methacrylate, ethyl acrylate, and methyl acrylate onto gelatin, G has a maximum with increasing reaction time.

Effect of Temperature. Temperature has multiple effects in this reaction system (Fig. 3). Raising the temperature increased the rate of graft copolymerization (R_g), and with it G. However, temperature can also increase the rate of homopolymerization (R_h), and at higher temperatures the increasing R_h will exceed R_g. That is why E decreased steadily and G decreased above 60°C. The decrease in E with rising temperature may also be attributed to

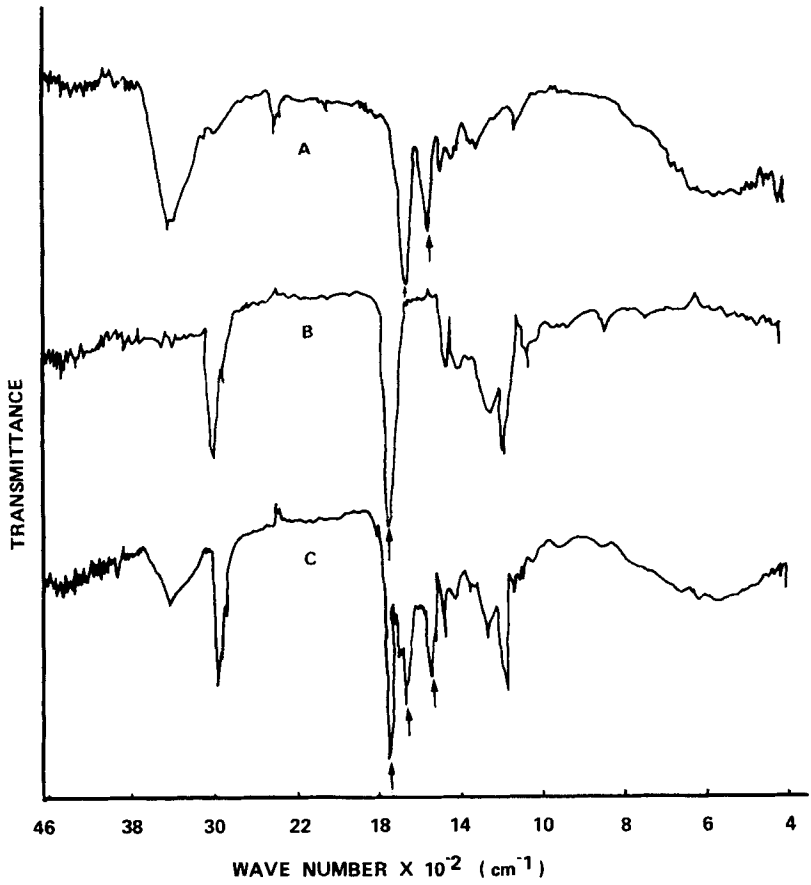


FIG. 1. IR spectra of pure gelatin (A), homo-PBA (B), and gelatin-*g*-PBA (C).

the solubility of monomer in the aqueous phase at higher temperatures, thus increasing the possibility of the monomer to contact Ce(IV), hence more Ce(IV) will be available to initiate the homopolymerization. In addition, at higher temperatures various chain-transfer processes are accelerated that lead to decreases in G and E.

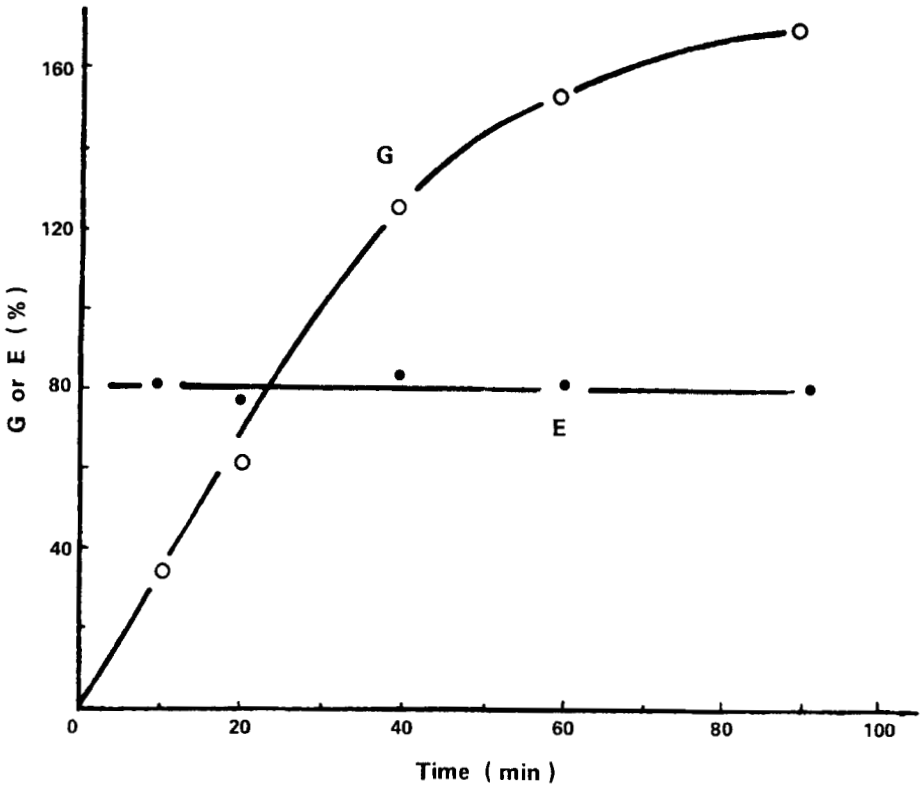


FIG. 2. Effect of time on grafting. [Gelatin] = 1.515×10^{-4} mol/L, [BA] = 0.234 mol/L, [CAN] = 7.5×10^{-3} mol/L, [HNO_3] = 0.042 mol/L, 60°C.

Effect of Monomer Concentration. With an increase in monomer concentration [M], G increased and E decreased (Fig. 4). The rapid increase in G at lower [M] is due to the fact that the rate of graft copolymerization R_g increases with increasing monomer concentration (see Eqs. 21 and 24 below). But with higher monomer concentrations, Ce(IV) will preferably initiate more monomer, leading to more homopolymer formation, decreasing E.

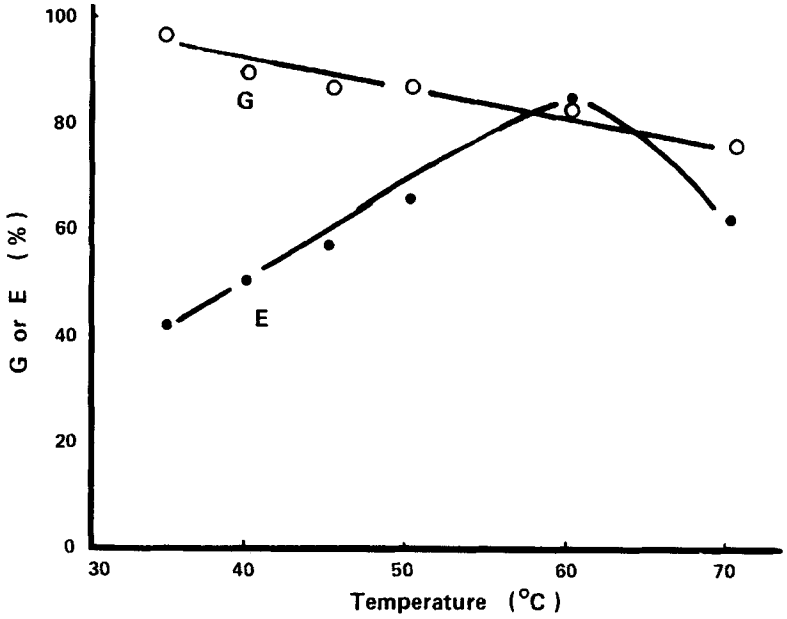


FIG. 3. Effect of temperature on grafting. [Gelatin] = 1.515×10^{-4} mol/L, [BA] = 0.351 mol/L, [CAN] = 7.5×10^{-3} mol/L, [HNO_3] = 0.042 mol/L, time = 20 min.

Effect of Gelatin Concentration. As shown in Fig. 5, with increasing gelatin concentration, *G* decreased steadily and *E* had a maximum. It may be explained that, although the weight of the grafted side chains may increase with the increase in gelatin concentration and cause *E* to increase, the decrease in the monomer-to-backbone ratio lowers *G*. When the gelatin concentration was increased further, the rate of graft copolymerization may have been hindered by the high viscosity of the reaction system. Besides, high gelatin concentrations can produce more gelatin macroradicals, which can interact with each other to terminate the reaction, thus lowering both *G* and *E*.

Effect of Initiator Concentration. Figure 6 indicates that, with increasing Ce(IV) concentration, *G* and *E* both increased and reached a maximum value at a Ce(IV) concentration of 7.49 mmol/L. With a further increase in Ce(IV) concentration, *G* and *E* decreased, possibly because at lower initiator concentrations, the Ce(IV) ions were mainly used to initiate the gelatin macromole-

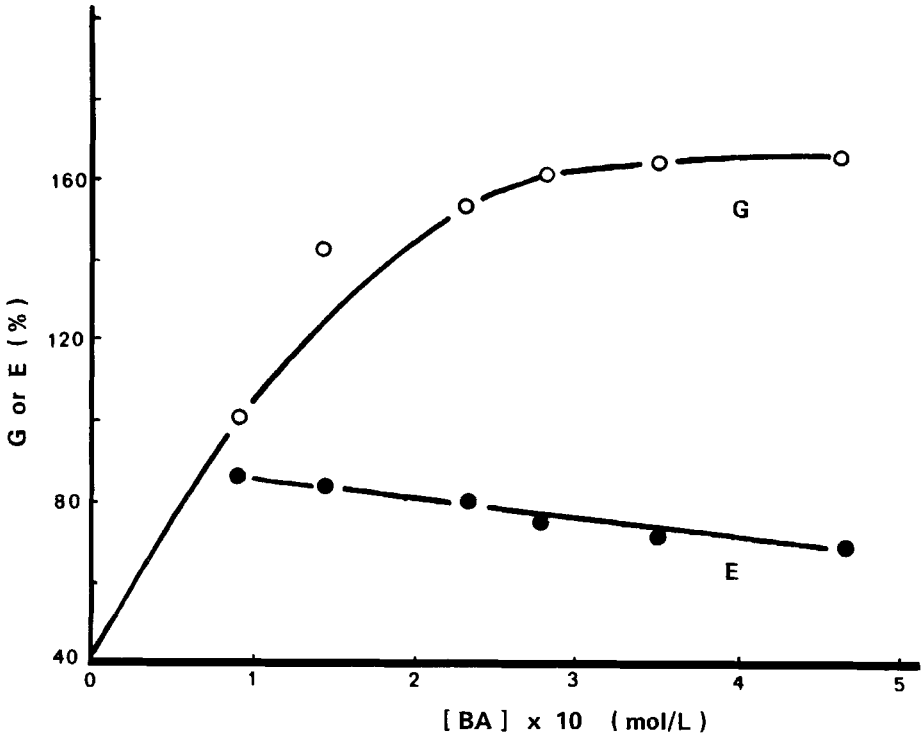


FIG. 4. Effect of [BA] on grafting. [Gelatin] = 1.515×10^{-4} mol/L, [CAN] = 7.5×10^{-3} mol/L, [HNO_3] = 0.042 mol/L, 60°C, time = 1 h.

cules, thus increasing the R_g. On the other hand, at lower initiator concentrations the reaction is mostly terminated by the recombination of double radicals, and R_g is proportional to the square root of [CAN] (see Eq. 21 below), so that G increases with increasing [CAN]. But at higher [CAN], the growing grafted polymeric chains may be easily terminated by Ce(IV) (oxidizing reaction), thus lowering G and E.

Effect of Acid Concentration. In the Ce(IV)-initiated grafting reactions, a small amount of mineral acid was found to be the catalyst for graft copolymerization. It was observed from Fig. 7 that there is an optimum concentration of nitric acid (0.042 mol/L), at which the best G and E can be

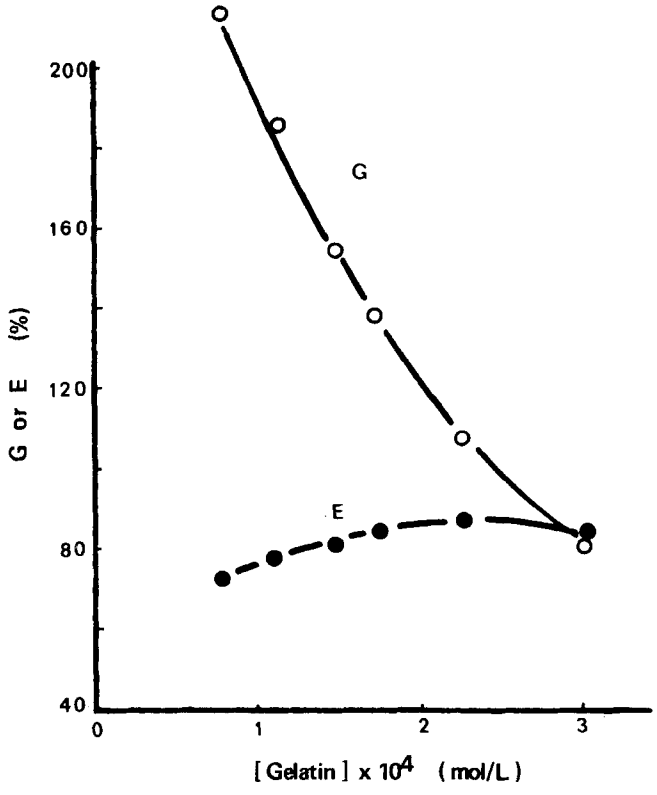


FIG. 5. Effect of [gelatin] on grafting. [BA] = 0.234 mol/L, [CAN] = 7.5×10^{-3} mol/L, [HNO_3] = 0.042 mol/L, 60°C, time = 1 h.

achieved. In the meantime, it is of interest to note that, without nitric acid in the system, graft copolymerization does not occur ($G = 0$). This may be explained as follows:

$$Ce^{4+} + H_2O \rightleftharpoons (CeOH)^{3+} + H^+, \quad (1)$$

$$2(CeOH)^{3+} \rightleftharpoons (Ce{-}O{-}Ce)^{6+} + H_2O. \quad (2)$$

Three types of ceric ion, Ce^{4+}, $(CeOH)^{3+}$ and $(Ce{-}O{-}Ce)^{6+}$, exist in aqueous solution, and the concentration of these species was found to vary with the

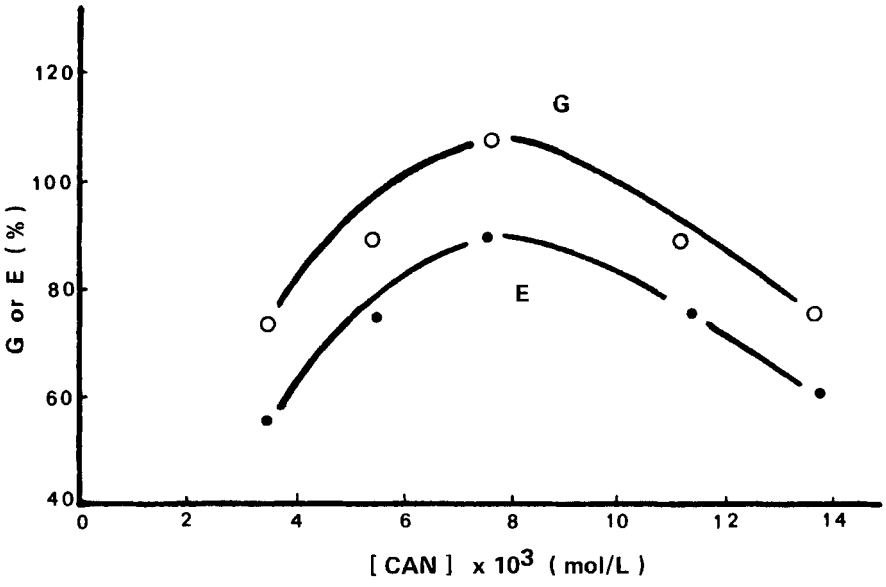


FIG. 6. Effect of [CAN] on grafting. [Gelatin] = 2.2727×10^{-4} mol/L, [BA] = 0.234 mol/L, [HNO_3] = 0.042 mol/l, 60°C, time = 1 h.

concentration of acid. As $(CeOH)^{3+}$ and $(Ce{-}O{-}Ce)^{6+}$ cannot initiate the graft copolymerization because of steric hindrance, Ce^{4+} is the only ion to initiate grafting. In the absence of nitric acid, Reactions (1) and (2) will shift toward the right, and few Ce^{4+} species exist, resulting in zero grafting. When nitric acid is added to the system, the above two reactions will be shifted to the left, thus producing more Ce^{4+}, which can initiate the reaction, and *G* and *E* increase. But at acid concentrations beyond the optimum point, not only more Ce^{4+} ions are produced, but also more H^+. Since they are both terminating agents, *G* and *E* decrease.

Effect of Inorganic Salts. It was found that (Table 1) the addition of $CuSO_4$ and K_2SO_4 will greatly decrease *G*, especially $CuSO_4$ acted as a polymerization inhibitor. It may be thought that an electron-transfer occurred between Cu^{2+} and the free radical, destroying the growing radicals:

$$-M^{\cdot} + Cu^{2+} \longrightarrow -M + Cu^{+}.$$

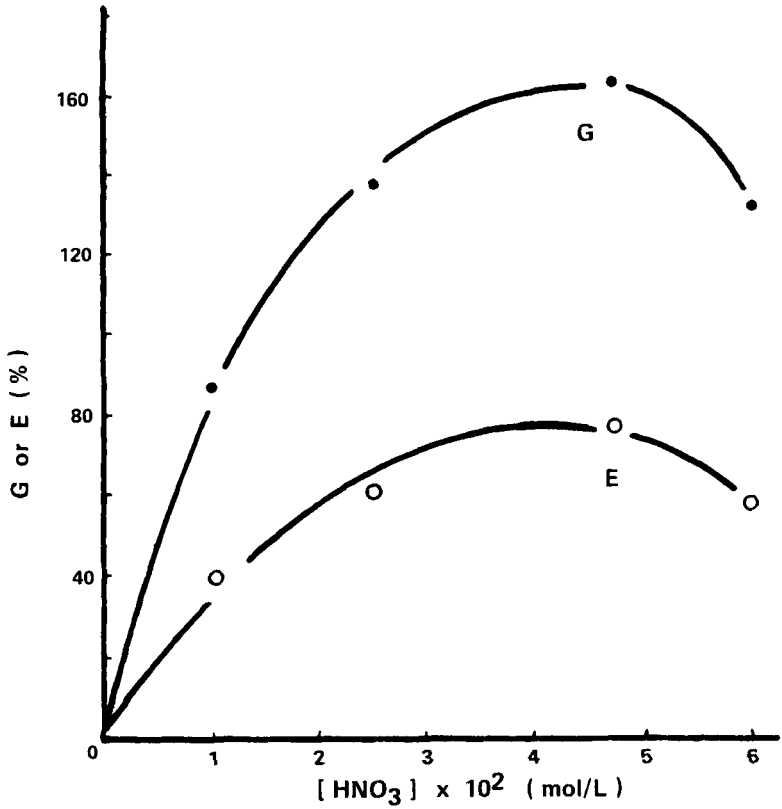


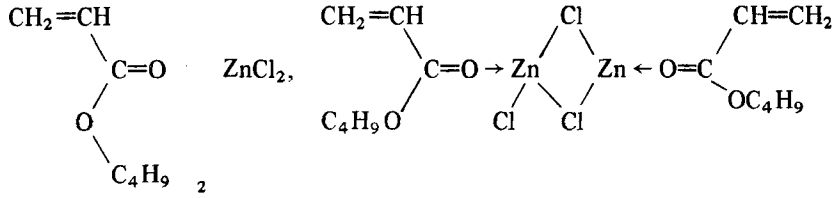
FIG. 7. Effect of $[HNO_3]$ on grafting. [Gelatin] = 1.515×10^{-4} mol/L, [BA] = 0.351 mol/L, [CAN] = 7.5×10^{-3} mol/L, 60°C, time = 1 h.

TABLE 1. Effect of Inorganic Salts on Grafting[a]

Inorganic salts	Concentration, mol/L	*G*, %	*E*, %
$CuSO_4$	0.02	0	0
K_2SO_4	0.02	27.7	85.2
$ZnCl_2$	0.02	71.7	84.0
Blank	—	60.7	93.0

[a]Conditions: [Gelatin] = 1.515×10^{-4} mol/L, [BA] = 0.351 mol/L, [CAN] = 7.5×10^{-3} mol/L, $[HNO_3]$ = 0.04 mol/L, 35°C, time = 20 min.

Addition of $ZnCl_2$ to the reaction system can increase G and decrease E. This effect may be attributed to the formation of a complex between the polar group of butyl acrylate and the metal halide, resulting in an increase in reactivity of the complexed monomer.



2:1 BA-$ZnCl_2$ complex 1:1 BA-$ZnCl_2$ complex

When the amount of BA in the reaction system is sufficient, the complexed monomer will accelerate the graft copolymerization and the homopolymerization, thus increasing G and decreasing E.

Effect of Organic Additives. Misra et al. studied the effect of amines on the graft copolymerization of ethyl acrylate on gelatin [16]. We have found that the addition of a small amount of methanol or ethylene glycol can enhance the rate of polymerization, but E decreased with increasing amount of ethylene glycol (Table 2).

TABLE 2. Effect of Organic Additives on Grafting[a]

Organic additives	Concentration, mol/L	Conversion of monomer, %	G, %	E, %
Methanol	0.156	44.5	92.5	80.1
Ethylene glycol	0.1875	26.9	57.0	81.5
	0.7813	46.7	67.6	55.8
	1.5625	58.8	69.1	45.3
Blank	–	25.0	41.1	94.2

[a]Other conditions as in Table 1.

TABLE 3. Effect of Emulsifier on Grafting[a]

	Conversion of monomer, %	*G*, %	*E*, %
With OP-10	73.6	160.9	84.2
Blank	25.0	41.6	94.2

[a]Other conditions as in Table 1.

McDowall et al. proposed that Ce(IV) can form a complex with alcohols to produce free radicals that initiate the polymerization [15], e.g.,

$$\text{Ce(IV)} + \text{A} \longrightarrow \text{A}^{\cdot} + \text{Ce(III)} + \text{H}^{+},$$

$$\text{A}^{\cdot} + \text{BA} \longrightarrow \text{A–BA}^{\cdot},$$

where A represents the organic additive.

It was obvious that the total conversion of monomer will be increased by the addition of these compounds. As the organic additive free radicals can also initiate the gelatin macromolecules, the rate of graft copolymerization and homopolymerization will be increased, thus resulting in an increase in *G* and decrease in *E*.

Effect of Emulsifier. Table 3 shows the effect of emulsifier (OP-10) on grafting. Because this nonionic emulsifier can raise the rate of graft copolymerization, *G* was increased. At the same time, more homopolymer was formed, so the total conversion of monomer increased and *E* decreased.

In this system the product is a stable emulsion, it can be used directly for making light-sensitive film.

The Disappearance Rate of Ceric Ion

The disappearance rate of Ce(IV) in the reaction system will help us to learn more about the graft copolymerization of BA onto gelatin.

Because the tetravalent cerium has a coordination number of six and gelatin has a lot of reactive groups, the formation of a complex is possible. The following mechanism of initiation was proposed by many authors [8, 9, 17, 18]:

$$\text{Ce(IV)} + \text{Gel} \underset{}{\overset{K}{\rightleftharpoons}} \text{Gel–complex} \xrightarrow{k_d} \text{Gel}^{\cdot} + \text{Ce(III)} + \text{H}^{+}, \qquad (3)$$

where Gel represents gelatin. The disappearance rate of Ce(IV) due to Eq. (3) may be written

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_d K[\text{Gel}][\text{Ce(IV)}]}{1 + K[\text{Gel}]} . \tag{4}$$

Similarly, the monomer BA also may form a complex with Ce(IV):

$$\text{Ce(IV)} + \text{BA} \underset{}{\overset{K'}{\rightleftharpoons}} \text{BA–complex} \xrightarrow{k_d'} \text{BA}^{\cdot} + \text{Ce(III)} + \text{H}^{+}. \tag{5}$$

The disappearance rate of Ce(IV) due to Eq. (5) is

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_d K'[\text{BA}][\text{Ce(IV)}]}{1 + K'[\text{BA}]} . \tag{6}$$

The total disappearance rate of Ce(IV), R_c, may be considered as the sum of Eqs. (4) and (6):

$$R_c = \left(\frac{k_d K[\text{Gel}]}{1 + K[\text{Gel}]}\right) + \left(\frac{k_d' K'[\text{BA}]}{1 + K'[\text{BA}]}\right)[\text{Ce(IV)}] . \tag{7}$$

In order to illustrate Eq. (7), another set of experiments with short reaction times was undertaken. The results are tabulated in Table 4.

Effect of Initiator Concentration. Table 4 (No. 1) and Fig. 8 show the effect of [CAN] on R_c. A straight line passing through the origin is observed. This indicates that R_c is directly proportional to the initial concentration of Ce(IV), and agrees with Eq. (7).

Effect of the Concentration of Gelatin and Monomer. Figure 9 shows the effect of gelatin concentration on R_c. It was observed that, at lower gelatin concentrations, R_c is directly proportional to gelatin concentration. But from Eq. (7) it is obvious that, when [Ce(IV)] and [BA] are fixed, the relationship between R_c and [Gel] will not always be a linear one. Only when K is very small and $1 + K[\text{Gel}] \approx 1$ can a straight line be obtained. Besides, there is another possibility that results in a linear relationship, i.e., no complex is formed between Ce(IV) and gelatin, and the free radicals are produced by a one-electron transfer process:

TABLE 4. Factors Influencing the Rate of Disappearance of Ce(IV)

No.	Factors		$R_c \times 10^6$, mol/(L·s)	Other conditions
1	[CAN] $\times 10^3$, mol/L	1.671	6.592	[Gel] = 0.7576×10^{-4} mol/L
		2.955	14.053	[BA] = 0.156 mol/L
		4.134	17.289	[HNO_3] = 0.04 mol/L
		5.440	25.502	Temperature = 40 ± 0.1°C
				Time = 5 min
2	[Gel] $\times 10^4$, mol/L	0	1.233	[BA] = 0.156 mol/L
		0.3939	3.453	[CAN] = 3.65×10^{-3} mol/L
		0.7576	4.989	[HNO_3] = 0.04 mol/L
		1.5152	8.607	Temperature = 35 ± 0.1°C
		2.2727	10.667	Time = 5 min
3	[BA], mol/L	0	0	[Gel] = 0
		0.156	1.233	[CAN] = 3.65×10^{-3} mol/L
		0.280	1.921	[HNO_3] = 0.04 mol/L
		0.420	2.908	Temperature = 35 ± 0.1°C
		0.560	3.947	Time = 5 min

$$\text{Ce(IV)} + \text{Gel} \longrightarrow \text{Gel}^{\cdot} + \text{Ce(III)} + \text{H}^{+}. \quad (8)$$

At higher gelatin concentrations the relationship seems to deviate from a straight line. This may be due to the formation of a certain amount of complex or to the increasing viscosity at higher gelatin concentrations, which hinders the polymerization, as discussed above.

The plot in Fig. 9 not passing through the origin may indicate that gelatin and monomer were both involved in the initiating reactions (see Eqs. 3 and 5). In order to prove this, the polymerization of butyl acrylate with Ce(IV) was carried out in the absence of gelatin [Table 4 (No. 3) and Fig. 10]. It was

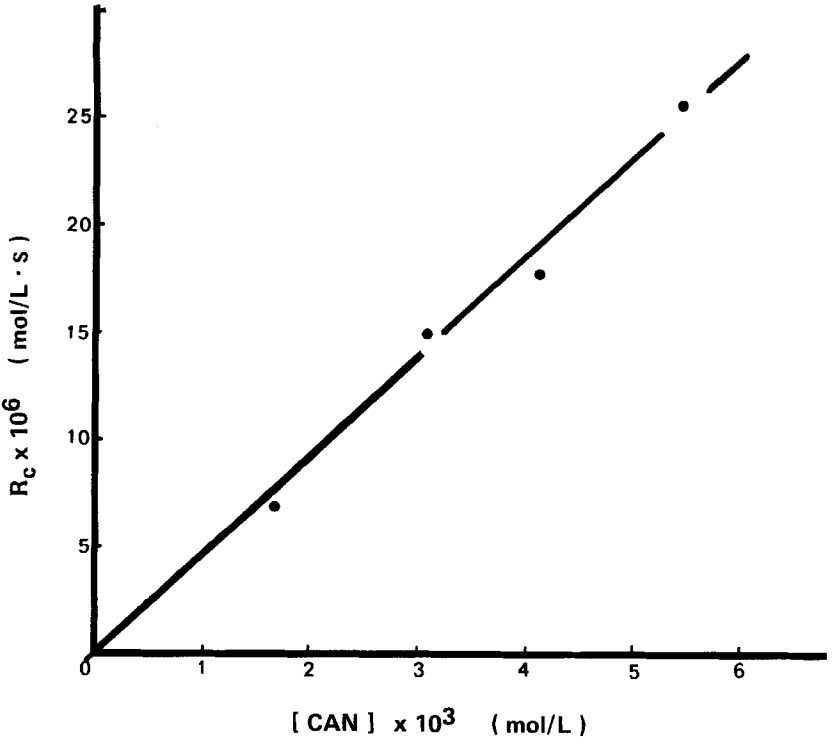


FIG. 8. Effect of [CAN] on R_c.

observed that the relationship between R_c and [BA] is a straight line through the origin proving that BA is involved in the initiating reaction. Furthermore, the straight line in Fig. 10 also confirms that there is no complex formed between Ce(IV) and BA. Hence, the initiation of BA may be considered to be

$$\text{Ce(IV)} + \text{BA} \xrightarrow{k_i'} \text{BA}^{\bullet} + \text{Ce(III)} + \text{H}^{+}. \tag{9}$$

Kinetics and Mechanism

The mechanism of this graft copolymerization is expected to proceed according to following scheme [8, 9].

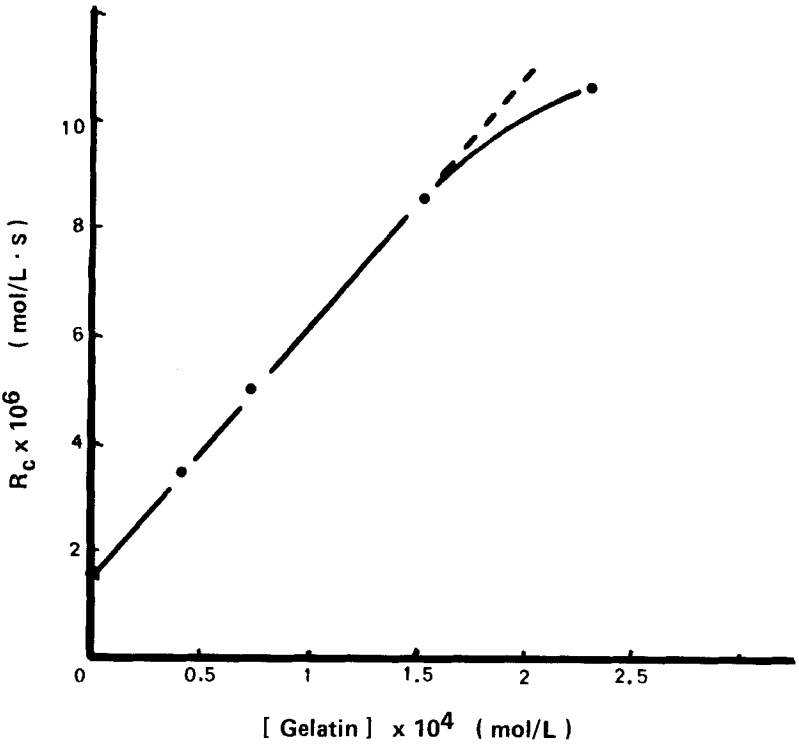


FIG. 9. Effect of [gelatin] on R_c.

Initiation

$$\text{Ce(IV)} + \text{Gel} \underset{}{\overset{K}{\rightleftharpoons}} \text{Gel–complex} \xrightarrow{k_d} \text{Gel}^{\cdot} + \text{Ce(III)} + \text{H}^{+}, \quad (10)$$

$$\text{Gel}^{\cdot} + \text{M} \xrightarrow{k_i} \text{GelM}^{\cdot}, \quad (11)$$

$$\text{Ce(IV)} + \text{M} \xrightarrow{k_i'} \text{M}^{\cdot} + \text{Ce(III)} + \text{H}^{+}. \quad (12)$$

Propagation

$$\text{GelM}^{\cdot} + n\text{M} \xrightarrow{k_p} \text{GelM}_{n+1}^{\cdot}, \quad (13)$$

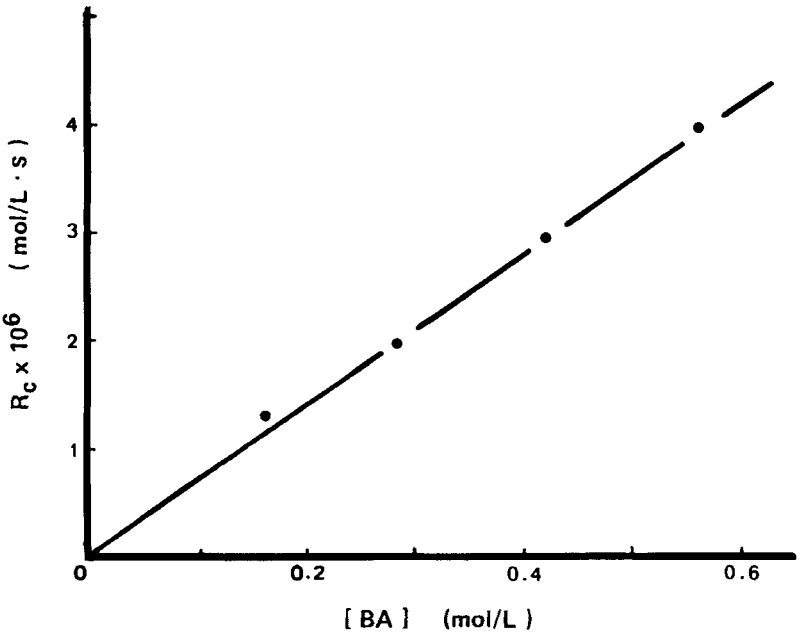


FIG. 10. Effect of [BA] on R_c.

$$M^{\cdot} + mM \xrightarrow{k_p'} M^{\cdot}_{m+1}. \tag{14}$$

Termination. Two types of termination may take place: (1) At lower Ce(IV) concentrations, the growing chain is terminated by the recombination of double radicals:

$$GelM_n^{\cdot} + GelM_n^{\cdot} \xrightarrow{k_{t_1}} \text{dead polymer}, \tag{15}$$

$$M_m^{\cdot} + M_m^{\cdot} \xrightarrow{k_{t_1}'} \text{dead polymer}, \tag{16}$$

$$GelM_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_{t_1}''} \text{dead polymer}. \tag{17}$$

(2) At higher Ce(IV) concentrations, the growing chain is terminated by a single radical:

$$\text{GelM}_n^{\cdot} + \text{Ce(IV)} \xrightarrow{k_{t_2}} \text{GelM}_n + \text{Ce(III)}, \tag{18}$$

$$\text{M}_m^{\cdot} + \text{Ce(IV)} \xrightarrow{k_{t_2}'} \text{M}_m + \text{Ce(III)}, \tag{19}$$

$$\text{Gel}^{\cdot} + \text{Ce(IV)} \xrightarrow{k_0} \text{oxidation products} + \text{Ce(III)}, \tag{20}$$

where M is monomer and Gel is gelatin.

It is postulated that $k_p = k_p'$, $k_{t_1} = k_{t_1}''$, $k_{t_2} = k_{t_2}'$ by using the three basic hypotheses in free-radical polymerization. Then the equation for the rate of polymerization can be obtained as follows.

For the case of double radical termination, assuming steady state, the rate of graft copolymerization R_g is given by

$$R_g = \frac{k_p k_d^{0.5} K}{k_{t_1}^{0.5}} \frac{[\text{Gel}]\,[\text{M}]\,[\text{Ce(IV)}]^{0.5}}{k_d K[\text{Gel}] + k_i[\text{M}]^{0.5}}, \tag{21}$$

the rate of homopolymerization R_h is

$$R_h = \frac{k_p k_i'}{k_{t_1}^{0.5}} \frac{[\text{M}]^2[\text{Ce(IV)}]^{0.5}}{(k_d K[\text{Gel}] + k_i[\text{M}])^{0.5}}, \tag{22}$$

and the total rate of polymerization R_p would be

$$R_p = R_g + R_h. \tag{23}$$

Similarly, for the case of single radical termination,

$$R_g = \frac{k_p k_d K}{k_{t_2}} \frac{[\text{M}]^2[\text{Gel}]}{[\text{M}] + (k_0/k_i)[\text{Ce(IV)}]}, \tag{24}$$

$$R_h = \frac{k_p k_i'}{k_{t_2}} [\text{M}]^2, \tag{25}$$

$$R_p = R_g + R_h = \frac{k_p}{k_{t_2}} [\text{M}]^2 \left\{ \frac{k_d K[\text{Gel}]}{[\text{M}] + (k_0/k_i)[\text{Ce(IV)}]} + k_i' \right\}. \tag{26}$$

TABLE 5. Effect of [CAN][a]

[CAN] X 10^3, mol/l	3.46	5.38	7.49	11.23	13.64
G, %	71.0	89.0	108.2	89.8	76.1
R_g X 10^5, mol/(L·s)	4.62	5.79	6.97	5.85	4.95

[a]Other conditions as in Fig. 6.

The above discussion can be more or less illustrated by the data in Table 5. From these data and Fig. 11, the effect of [CAN] on R_g can be seen. The plot of R_g vs $[CAN]^{0.5}$ is linear at lower [CAN], which agrees with termination by recombination of double radicals (Eq. 21). But at higher [CAN], the plot deviates from linearity. This may be due to single radical termination (Eq. 24) which decreases the rate of graft copolymerization.

Similar behavior was observed in Table 6 and Fig. 12. The relationship between R_g and [BA] in the lower [BA] region is nearly linear. Since the solubility of BA in water is limited, a further increase of [BA] makes little contribution to R_g.

Table 7 shows the effect of gelatin concentration on R_g, and Fig. 13 is a

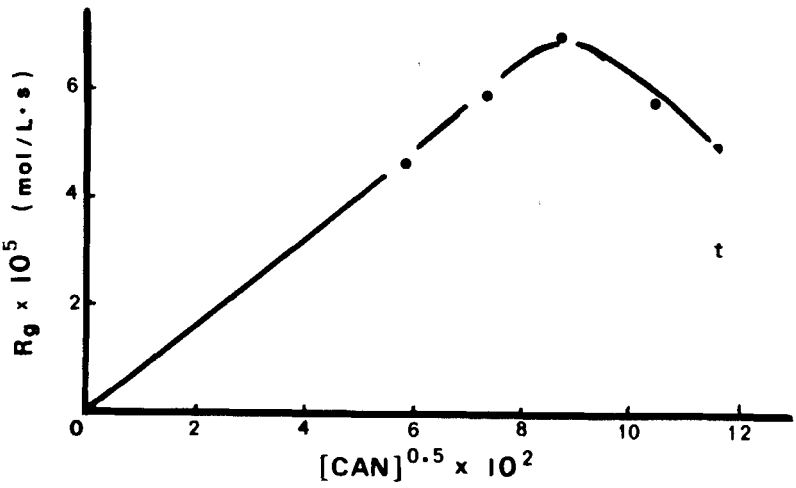


FIG. 11. Plot of R_g vs $[CAN]^{0.5}$.

TABLE 6. Effect of [BA][a]

[BA], mol/L	0.094	0.14	0.234	0.281	0.351	0.468
G, %	100.5	143.4	155.0	161.2	163.5	167.1
$R_g \times 10^5$, mol/(L·s)	4.36	6.22	6.73	6.99	7.09	7.25

[a]Other conditions as in Fig. 4.

plot of R_g vs $[Gel]^{0.5}$. At lower [Gel], there is a linear relation between R_g and $[Gel]^{0.5}$.

The effect of temperature on the rate of reaction was observed within the range of 35 to 70°C (Table 8). The log of the reaction rates were plotted according to the Arrhenius equation (Figs. 14 and 15) to obtain the apparent

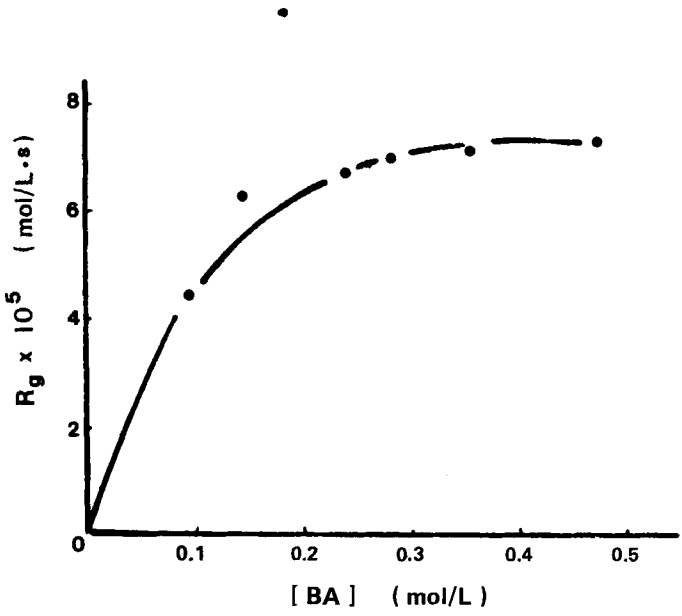


FIG. 12. Plot of R_g vs [BA].

TABLE 7. Effect of [Gelatin][a]

[Gel] $\times 10^4$, mol/L	0.7575	1.1363	1.5150	1.7424	2.2727	3.0303
G, %	214.1	186.5	155.0	139.3	108.2	81.0
$R_g \times 10^5$, mol/(L·s)	4.65	6.05	6.73	7.05	6.97	7.03

[a]Other conditions as in Fig. 5.

TABLE 8. Effect of Temperature on the Reaction Rates[a]

Temperature, °C	35	40	45	50	60	70
G, %	41.6	50.6	57.7	65.3	85.8	61.4
E, %	91.6	89.9	87.0	86.5	85.1	74.5
$R_g \times 10^4$, mol/(L·s)	2.167	2.136	3.004	3.403	4.466	3.198
$R_h \times 10^4$, mol/(L·s)	0.199	0.296	0.448	0.533	0.781	1.095
$R_p \times 10^4$, mol/(L·s)	2.365	2.932	3.452	3.936	5.247	4.293

[a]Other conditions as in Fig. 3.

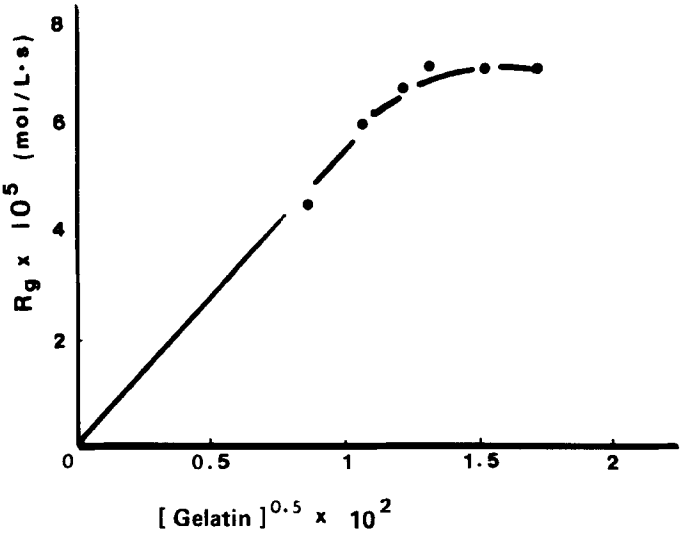


FIG. 13. Plot of R_g vs [gelatin]$^{0.5}$.

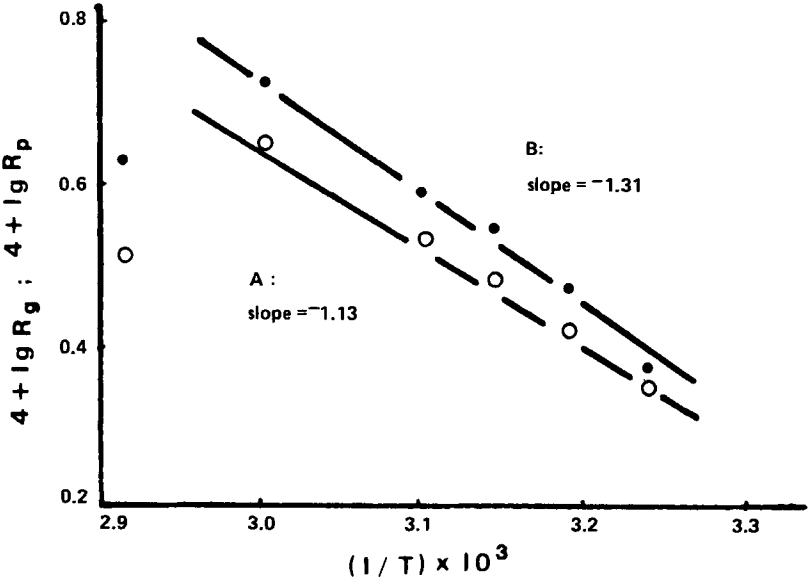


FIG. 14. A: Plot of lg R_g vs $1/T$. B: Plot of lg R_p vs $1/T$.

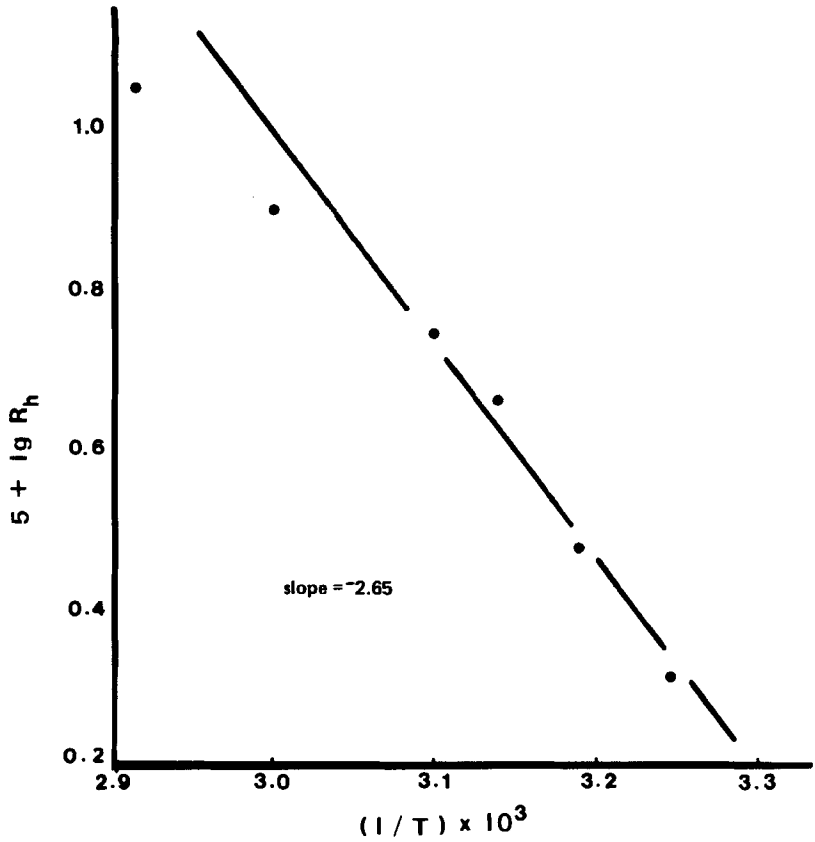


FIG. 15. Plot of lg R_h vs $1/T$.

activation energies for graft copolymerization (E_g), homopolymerization (E_h), and total polymerization (E_p):

E_g = 21.6 kJ/mol; E_h = 50.7 kJ/mol; E_p = 25.1 kJ/mol.

The activation energy for graft copolymerization is the lowest, which is why the grafting efficiency in the system studied here is relatively high. In general, higher grafting efficiency can be reached at lower reaction temperatures because raising the temperature will accelerate homopolymerization.

CONCLUSIONS

1. CAN can effectively initiate the graft copolymerization of BA onto gelatin.

2. The percentage of grafting and the grafting efficiency can be adjusted by varying the reaction temperature and the time, or the concentrations of gelatin, monomer, or initiator. The addition of $ZnCl_2$ can increase the rate of reaction.

3. In the system studied, the equilibrium constant for complex formation between gelatin and Ce(IV) was very small, or perhaps no complex was formed and the free radicals were produced directly by one-electron transfer.

4. At lower initiator concentrations, termination was caused mainly by recombination of double radicals. When the initiator concentration was higher, the termination was caused mainly by single radicals.

5. The apparent activation energies for graft copolymerization, homopolymerization, and total polymerization are 21.6, 50.7, and 25.1 kJ/mol, respectively.

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Received December 23, 1987
Revision received February 10, 1988