Grafting of Polymeric Side Chains to Gelatin

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Synopsis

Kinetics of grafting of poly(butyl acrylate) onto gelatin was studied with H_2O_2—ascorbic acid redox system. Percent grafting, grafting efficiency, R_g, and R_h were determined as a function of time, temperature, initiator, monomer, and backbone concentration. It was found that R_g depends on first power of monomer concentration and 0.5 power to the initiator concentrations. A detailed kinetic scheme is proposed to explain these results.

INTRODUCTION

Significant progress has been made recently in the chemical modification of industrial protinaceous materials to achieve improved physical and chemical properties.[1–6] The need for chemical techniques whereby the constitution of protein may be studied has stimulated an interest in reagents which will react with the protein molecules. The consequent effects that chemical modification have on the backbone of proteins has also interested the technologists. Gelatin has been recognized as a protein which can be particularly amenable to chemical activity. The number and the variety of reactive groups along the chain act as grafting sites. The present authors have recently reported on grafting of poly(butyl acrylate) on gelatin using potassium peroxydisulphate, a free radical initiator under a variety of conditions.[7] In this communication, grafting of poly(butyl acrylate) onto gelatin using hydrogen peroxide–ascorbic acid as initiators is reported as functions of reaction temperature, time, initiator, monomer, and backbone concentrations.

EXPERIMENTAL

Methods

Materials: Pure granular bacteriological sample of gelatin (BDH) was used. Butyl acrylate was freshly distilled, and the middle fraction was used. Hydrogen peroxide 6 vol % and ascorbic acid (BDH) were used without further purification.

Grafting Procedure

Grafting reactions were carried out in 100-mL reaction vessels with nitrogen inlet and outlet.[8] 10 mL of 10% gelatin solution was used. The concentrations of hydrogen peroxide and ascorbic acid was 10^{-2} and 10^{-3} mol/L, respectively. The required amount of butyl acrylate was used. The total volume was made

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up to 50 cc. The temperature of the reaction vessel was maintained at 60°C. After the completion of the reaction, the ingredients were poured into cold methanol and grafted gelatin was precipitated. The products were filtered, and then soxhlet was extracted. The kinetic parameters were calculated from gravimetric results.

RESULTS AND DISCUSSION

Grafting Efficiency (GE)

Grafting efficiency was computed gravimetrically from the weight of unbound homopolymer and total weight of polymer (unbound + bound):

$$\text{Grafting efficiency} = \frac{\text{wt grafted polymer}}{\text{wt homopolymer and wt of grafted polymer}}$$

All weights are expressed in grams. Grafting efficiency (GE) is defined as the weight fraction of the polymer grafted to the backbone and is therefore a measure of the extent of branching. In all the systems studied values of GE range from 0.5–0.9 (Tables I–V).

Grafting efficiency increases with backbone concentration initially since more backbone radicals would be produced with high concentration of gelatin resulting in more grafting. With further increase in backbone (BB) concentration, i.e., for the ratio of [BB]/[M] > 1, GE decreases. The decrease in GE is not clearly understood but may be attributable to the backbone radicals undergoing combination rather than initiating the polymerization of the monomers. Grafting efficiency increases initially with initiator concentration as the number of sites

TABLE I
Effect of Backbone Variation on R_p, R_h, R_g, GE, and Percentage Grafting

Backbone (g)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)	$R_h \times 10^6$ (mol/L/s)	$R_g \times 10^6$ (mol/L/s)	GE	% Grafting
0.7	44.57	11.59	0.810	10.78	0.93	53.21
0.8	69.06	17.96	0.509	17.45	0.97	75.38
1.0	—	7.33	1.29	6.05	0.82	20.91
1.2	33.51	8.71	2.09	6.62	0.76	19.08
1.5	10.02	2.60	0.51	2.09	0.97	5.49
2.0	2.59	0.67	0.38	0.29	0.43	0.50

Temp = 60°C; [M] = 0.18 mol/L; [H_2O_2] 1×10^{-2} mol/L; [AA] 1×10^{-3} mol/L.

TABLE II
Effect of Monomer Variation on R_p, R_h, R_g, GE, and Percentage Grafting

Monomer (M/L)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)	$R_h \times 10^6$ (mol/L/s)	$R_g \times 10^6$ (mol/L/s)	GE	% Grafting
0.18	44.07	11.46	3.39	8.06	0.70	27.86
0.36	50.68	26.35	11.09	15.25	0.58	52.73
0.54	56.97	44.44	24.38	20.66	0.45	69.34
0.72	65.34	67.96	24.41	43.55	0.64	150.52
0.89	61.16	79.51	34.74	44.77	0.56	154.73

Temp = 60°C; [H_2O_2] 1×10^{-2} mol/L; [AA] 1×10^{-3} mol/L; time = 90 min; backbone = 1 g.

TABLE III
Effect of Initiator Variation on R_p, R_h, R_g, GE and Percentage Grafting

Initiator, (H_2O_2) (mol/L)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)	$R_h \times 10^6$ (mol/L/s)	$R_g \times 10^6$ (mol/L/s)	GE	% Grafting
0.6×10^{-2}	13.69	3.56	0.04	3.52	0.99	12.15
1×10^{-2}	30.32	7.89	0.04	7.84	0.99	27.10
1.6×10^{-2}	—	—	1.49	12.60	0.89	43.56
2.0×10^{-2}	39.33	10.23	4.01	—	—	21.48
2.4×10^{-2}	41.04	10.69	0.14	10.55	0.98	36.39
3.0×10^{-2}	49.85	12.96	1.00	11.95	0.92	41.32

Temp = 60°C; (M) = 0.18 mol/L; backbone = 1 g; ratio of (AA)/(H_2O_2) = 0.1.

grafted are increased. With further increase in [I], the homopolymerization is also increased with reduction in grafting efficiency (Table III). Increase in time increases the GE. Since the gelatin backbone is active, the homopolymerization is less preferred to grafting, as seen in Table IV.

Rate of Grafting (R_g)

The rate of graft copolymerization R_g was calculated from the following expression:

$$R_g = R_p - R_h$$

TABLE IV
Effect of Time Variation on R_p, R_h, R_g, GE, and Percentage Grafting

Time (min)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)	$R_h \times 10^6$ (mol/L/s)	$R_g \times 10^6$ (mol/L/s)	GE	% Grafting
30	21.95	17.12	5.14	11.98	0.69	13.80
60	38.96	15.20	2.69	12.51	0.82	28.81
90	44.84	11.61	2.16	9.45	0.81	32.68
120	31.18	6.08	1.26	4.82	0.79	22.20
180	23.81	3.09	1.46	1.63	0.52	11.28
210	19.71	5.33	0.32	5.01	0.94	—

Temp = 60°C; (M) = 0.18 mol/L; (H_2O_2) 1×10^{-2} mol/L; (AA) 1×10^{-3} mol/L; backbone = 1 g.

TABLE V
Effect of Temperature Variation on R_p, R_h, R_g, GE, and Percentage Grafting

Temp (°C)	Conversion (%)	$R_p \times 10^6$ (mol/L/s)	$R_h \times 10^6$ (mol/L/s)	$R_g \times 10^6$ (mol/L/s)	GE	% Grafting
30	55.78	14.51	4.49	10.01	0.68	34.58
40	51.98		13.51	1.47	12.04	0.89
41.64						
50	51.30	13.34	1.41		11.93	0.89
41.22						
60	41.67		10.83	1.76	9.07	0.83
31.35						
70	38.38	9.98	1.39	8.58	0.86	29.66
80	39.96	10.40	1.97	8.43	0.81	29.12

Time = 90 min; (M) = 0.18 mol/L; (H_2O_2) = 1×10^{-2} mol/L; (AA) = 1×10^{-3} mol/L; backbone = 1 g.

R_g decreases with increase in backbone (Table I) concentration, showing that as the concentration of the backbone is increased; deactivation of backbone radical may occur through combination or interaction with primary radicals. R_g depends on first power of monomer concentration (Table II, Fig. 1) and 0.5 power on initiator concentration (Table III, Fig. 2).

In the beginning R_g increases and then decreases (Table IV) with time. The slower rate of grafting could be due to depletion in monomer concentration and also due to the shortage of available grafting sites as the reaction proceeds.

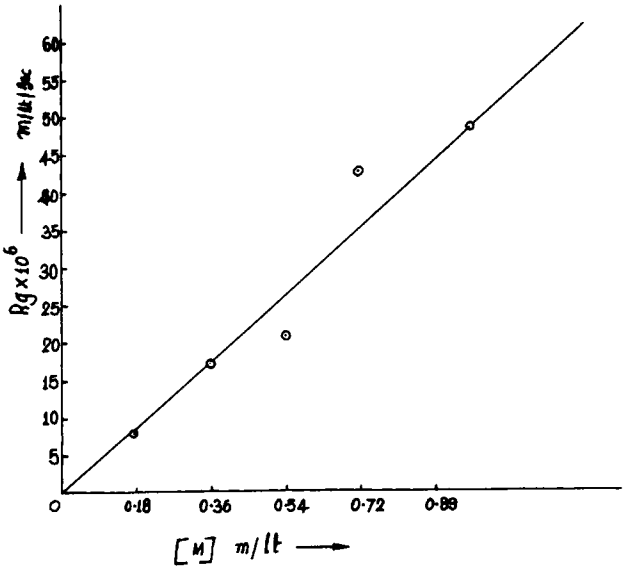

Fig. 1. Effect of monomer variation on R_g. Temp = 60°C; $(H_2O_2) = 1 \times 10^{-2}$ mol/L; [AA] = 1×10^{-3} mol/L; time = 90 min; backbone = 1 g.

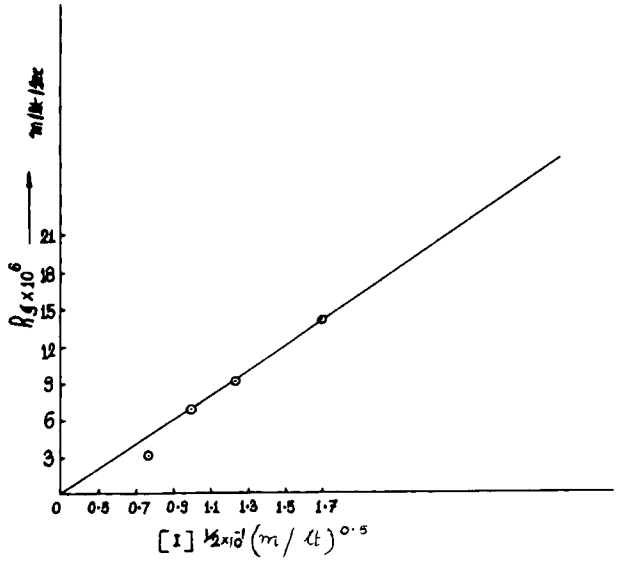

Fig. 2. Effect of initiator concentration on R_g. Temp = 60°C; [M] = 0.18 mol/L; backbone = 1 g; ratio of $[AA]/[H_2O_2] = 0.1$.

R_g decreases with increase in temperature (Table V) due to decrease in monomer and initiator concentration in the swollen phase as the rate of consumption of the monomer due to homopolymerization is also higher at higher temperatures.

Rate of Polymerization (R_p)

R_p was determined from the total weight of the polymer formed, i.e., weight of homopolymer + weight of the same polymer bound as graft side chains. This was equal to the weight of the polymer mixture obtained after graft polymerization reaction minus the initial weight of the backbone taken. The rate of polymerization was computed from the weight of the polymer:
rate of polymerization

$$R_p \text{ (mol/L/s)} = \frac{\text{wt of polymer} \times 1000}{\begin{pmatrix}\text{molecular}\\ \text{wt of}\\ \text{monomer}\end{pmatrix} \times \begin{pmatrix}\text{time of}\\ \text{polymeri-}\\ \text{zation (s)}\end{pmatrix} \times \begin{pmatrix}\text{vol of}\\ \text{reaction}\\ \text{mixture}\end{pmatrix}}$$

At first R_p increased with increase in backbone concentration and then decreased steadily (Table I). This may be due to the higher amount of homopolymer being formed.

Variation in initiator concentration was found to increase R_p initially and then decrease. The decrease in R_p with increasing initiator concentration may be due to annihilation of primary radicals formed in the system and also due to homopolymerization reactions.

R_p was found to increase with temperatures and then decrease. Thus an increase in reaction temperature favors homopolymerization rather than graft copolymerization.

A steady decrease of R_p with time shows that more of homopolymer is formed as time increases.

REACTION MECHANISM

Based on the above kinetics following scheme is proposed for the grafting reaction.

$$H_2O_2 + AA \xrightarrow{K_d} R\cdot$$

$$R\cdot + \text{gel} \xrightarrow{K_{i1}} \text{gel}\cdot$$

$$\text{gel}\cdot + M \xrightarrow{K_{i2}} \text{gel } M\cdot$$

$$\text{gel } M\cdot + M \xrightarrow{K_p} P\cdot$$

$$P\cdot + P\cdot \xrightarrow{K_t} \text{polymer}$$

$$\frac{d(R\cdot)}{dt} = 0 = K_d(H_2O_2)(AA) = K_{i1}(R\cdot)(\text{gel})$$

$$(R\cdot) = \frac{K_d(H_2O_2)\,(AA)}{(gel)K_{i1}}$$

$$K_{i1}(R\cdot)(gel) = K_{i2}(gel\cdot)(M)$$

$$(gel\cdot) = \frac{K_{i1}(R\cdot)(gel)}{K_{i2}(M)}$$

$$= \frac{K_{i1}K_d(H_2O_2)(AA)gel}{gel\,K_{i2}(M)}$$

$$= \frac{K_d(H_2O_2)(AA)}{K_{i2}(M)}$$

$$K_{i2}(gel\cdot)(M) = K_f(P\cdot)^2$$

$$(P\cdot) = \left(\frac{K_{i2}}{K_t}\right)^{1/2}(M)^{1/2}\left(\frac{K_d(H_2O_2)(AA)}{K_{i2}(M)}\right)^{1/2}$$

$$R_g = K_p\,(gel\,M\cdot)(M)$$

$$= K_p\left(\frac{K_{i2}}{k_t}\right)^{1/2}(M)\,\frac{[K_d(H_2O_2)(AA)]^{1/2}}{[K_{i2}(M)]^{1/2}} \times M^{1/2}$$

$$R_g = \frac{K_p}{K_t{}^{1/2}}M^{1.0}(K_dH_2O_2AA)^{1/2}$$

Decomposition of H_2O_2 most probably proceeds as shown by the following equation:

$$H_2O_2 \rightarrow \cdot OH + \cdot OH \tag{1}$$

The ·OH radical abstracts hydrogen from the gelatin backbone to yield a gelatin macroradical capable of initiating grafting as shown by

$$gel—OH + \cdot OH \rightarrow gel—O\cdot + H_2O \tag{2}$$

$$gel—O\cdot + M \rightarrow gel—O—M\cdot \tag{3}$$

$$gel—O—M\cdot + nM \rightarrow graft \tag{4}$$

where M is the vinyl monomer. These reactions proceed favorably up to certain H_2O_2 concentrations. Beyond this, ·OH radicals may largely participate in termination processes with the growing polymer chain, thus decreasing grafting efficiency.

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