Grafting of butyl acrylate onto gelatin in a water–isopropanol medium

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Graft copolymerization of butyl acrylate onto gelatin using potassium persulphate initiator was studied in a water–isopropanol medium. The crude graft copolymers were soxhlet extracted with acetone to remove the loosely bound ungrafted homopolymer. The influence of a number of experimental factors such as effect of time, monomer concentration, initiator concentration, backbone concentration and temperature on the graft copolymerization of gelatin were investigated.

(Keywords: grafting; gelatin; water–isopropanol medium; mechanism)

INTRODUCTION

Gelatin, a derived protein, which although not homogeneous, is chemically a well defined substance. The sequence of amino acid residues along the polypeptide chain of gelatin makes it amenable to chemical reactivity[1]. The solution medium regulates the length of the grafted chains and also minimizes any side reactions such as crosslinking of backbone radicals etc. In addition the resultant graft copolymer solution may be directly used for various application purposes[2]. Some kinetic parameters of the grafting butyl acrylate onto gelatin were studied at low conversion. In order to gain an insight into the mechanism of the grafting reaction, the effects of variation of reaction time, monomer concentration, initiator concentration, backbone concentration and temperature on grafting parameters have been studied.

EXPERIMENTAL

Materials

A pure granular bacteriological sample of gelatin (BDH) was used. Butyl acrylate (Rohm and Haas, USA) was freshly distilled and the middle fraction was used. Potassium peroxydisulphate (Riedel, Germany) was used as such without further purification.

Grafting procedure

Gelatin was dissolved in a water–isopropanol medium (1:1 v/v). This solution was used for all reactions. Grafting reactions were carried out in 100 ml reaction vessels with nitrogen inlet and outlet. A 10% gelatin solution (10 ml) was used and the requisite amounts of monomer and initiator were added. The temperature of the reaction vessel was maintained at 60°C. After the required time the ingredients were poured into ice cold methanol and grafted gelatin was precipitated. The products were filtered and then soxhlet extracted.

Isolation of the graft copolymer

The gross polymer obtained in the present case consists of unreacted gelatin, graft copolymer and unbound homopolymer poly(butyl acrylate) (PBA). In order to isolate the pure graft copolymer a selective solvent extraction method was used. The unbound butyl acrylate homopolymer was completely extracted with acetone. After 48 h, each sample was further extracted with fresh solvents until a constant value was obtained. The amount of apparent graft formation was obtained from the difference in weight of extracted and original specimens each weighed in a moisture free state. The kinetic results were calculated from the gravimetric results.

Grafting efficiency (*GE*) was computed gravimetrically from the weight of unbound homopolymer and total weight of polymer.

$$GE = \frac{\text{weight of grafted PBA}}{\text{weight of homo PBA} + \text{weight of grafted PBA}}$$

The rate of graft copolymerization R_g was calculated from the following expression. This is given by the amount of graft copolymers obtained from complete isolation of the free homopolymer.

$$R_g = R_p - R_h$$

where R_p = rate of total polymerization; R_h = rate of homopolymerization.

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

RESULTS AND DISCUSSION

Effect of reaction time

The effect of reaction time on percent grafting, grafting efficiency and rate of grafting is shown in *Table 1*. Percent grafting was found to increase with an increase in reaction time and then remained more or less constant. The increase in percent grafting is accounted for by the increase in number of grafting sites in the initial stages of the reaction[3]. Longer reaction periods have little effect on the degree of grafting due to the number of active sites

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Table 1 Effect of time on grafting

Time (min)	$R_g \times 10^6$ (mol l^{-1} s^{-1})	Grafting efficiency	Percent grafting
30	6.32	89.77	26.32
60	9.46	88.41	28.47
90	15.31	86.84	30.46
120	18.24	85.88	32.60
180	19.00	85.81	33.00
210	19.42	85.63	33.57

$[BA] = 1.404 \times 10^{-1}$ mol l^{-1}
$[KPS] = 10 \times 10^{-3}$ mol l^{-1}
$[Gelatin] = 3.3 \times 10^{-4}$ mol l^{-1}
Total volume = 50 ml
Temperature = 60°C

remaining almost constant with increasing grafting time and hence there is no further decrease in percent grafting[4]. It was observed that grafting efficiency did not change appreciably during the course of the reaction.

Effect of monomer concentration

There is a regular increase in percent grafting, grafting efficiency and rate of grafting with increase in monomer concentration (*Table 2* and *Figure 1*). This is due to the fact that propagation of growing grafted chains is facilitated in the presence of a higher concentration of monomer[5]. When compared with the aqueous system[6], rate of grafting, percent grafting and chain length values are lower and this may be due to the competitive reaction between isopropanol and gelatin for the primary radicals[7].

The plot of log R_g vs. log[BA] gave a slope value of 1.5 and R_g vs. $[BA]^{1.5}$ were straight lines passing through the origin (*Figure 1*). The increase in the kinetic orders of the rate of graft copolymerization in this system may be due to the heterogeneous nature of the system.

Effect of initiator concentration

An increase in initiator concentration from 6×10^{-3} mol l^{-1} to 3.0×10^{-2} mol l^{-1} increases the percent grafting and grafting efficiency (*Table 3* and *Figure 2*). When compared with the aqueous system the rates are lower and this could be explained in the light of the mechanism proposed by Ball *et al.*[7] for the reaction of isopropyl alcohol with persulphate ion. In the present system it is observed that the primary radicals attack the isopropyl alcohol to form isopropyl radicals hence the availability of primary radicals for the backbone may be less, resulting in less percent grafting and a lessening in the rate of grafting.

The initial plot of R_g *versus* $[KPS]^{0.5}$ was found to be a straight line passing through the origin and log R_g *versus* log[KPS] plot gave a slope value of half an order (*Figure 2*). Thus, the initial rates from these plots were found to be proportional to the half power of the initiator concentration.

Effect of backbone concentration

The concentration of gelatin was varied from 2.2×10^{-4} mol l^{-1} to 6.3×10^{-4} mol l^{-1}. The percent grafting and rate of grafting increased up to 3.8×10^{-4} mol l^{-1} and then decreased (*Table 4* and *Figure 3*). The decrease may be due to termination by gelatin graft radicals when the concentration of gelatin is increased.

The plot of log R_g *versus* log[G] (in the increasing region of the rate) gave a slope value of half an order for the system.

Effect of temperature

The dependence of the rate of grafting and percent grafting on temperature in the range 30°C–60°C (*Table 5*, *Figure 4*) could be ascribed to a greater activation energy and its diffusion rate. But beyond 60°C the percentage of grafting decreases probably due to acceleration of the termination process, which leads to formation of a higher amount of homopolymer[8].

Table 2 Effect of monomer concentration on grafting

$[BA] \times 10^1$ (mol l^{-1})	$R_g \times 10^6$ (mol l^{-1} s^{-1})	Grafting efficiency	Percent grafting
1.404	8.35	87.43	25.10
2.106	13.72	90.26	30.31
2.808	18.46	91.71	38.45
3.610	21.90	92.24	46.11
4.212	26.10	94.10	55.17

$[KPS] = 10 \times 10^{-3}$ mol l^{-1}
$[Gelatin] = 3.3 \times 10^{-4}$ mol l^{-1}
Total volume = 50 ml
Temperature = 60°C
Time = 90 min

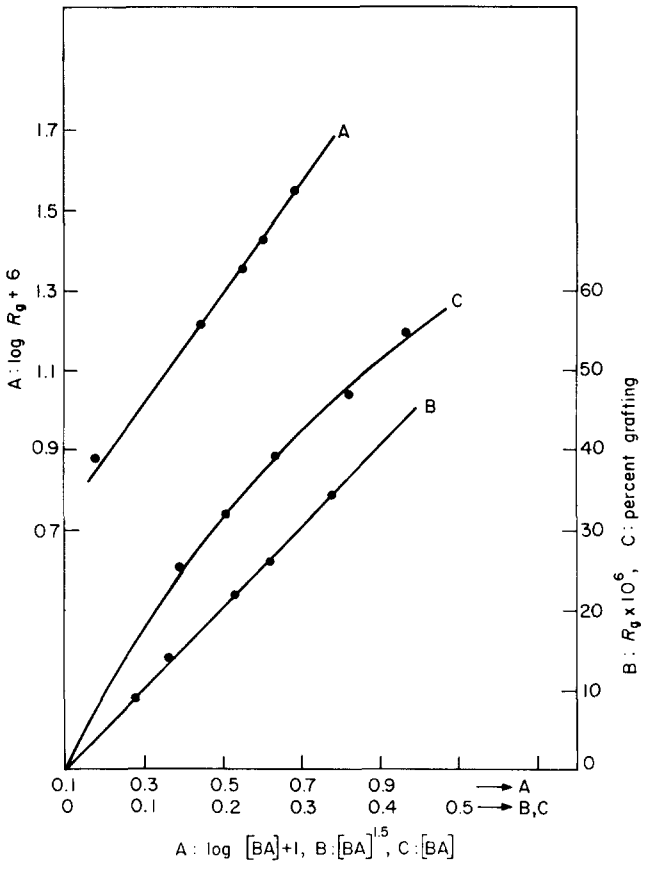

Figure 1 Effect of [monomer] on grafting: A, log R_g *versus* log[BA]; B, R_g *versus* $[BA]^{1.5}$; C, percent grafting *versus* [BA]

Table 3 Effect of initiator concentration on grafting

$[KPS] \times 10^3$ (mol l^{-1})	$R_g \times 10^6$ (mol l^{-1} s^{-1})	Grafting efficiency	Percent grafting
6	8.17	68.05	28.25
10	9.20	70.37	30.14
16	11.56	74.31	38.89
20	7.45	85.84	41.20
24	6.82	88.14	47.32
30	5.55	93.50	61.72

$[BA] = 1.4 \times 10^{-1}$ mol l^{-1}
$[Gelatin] = 3.3 \times 10^{-4}$ mol l^{-1}
Total volume = 50 ml
Temperature = 60°C
Time = 90 min

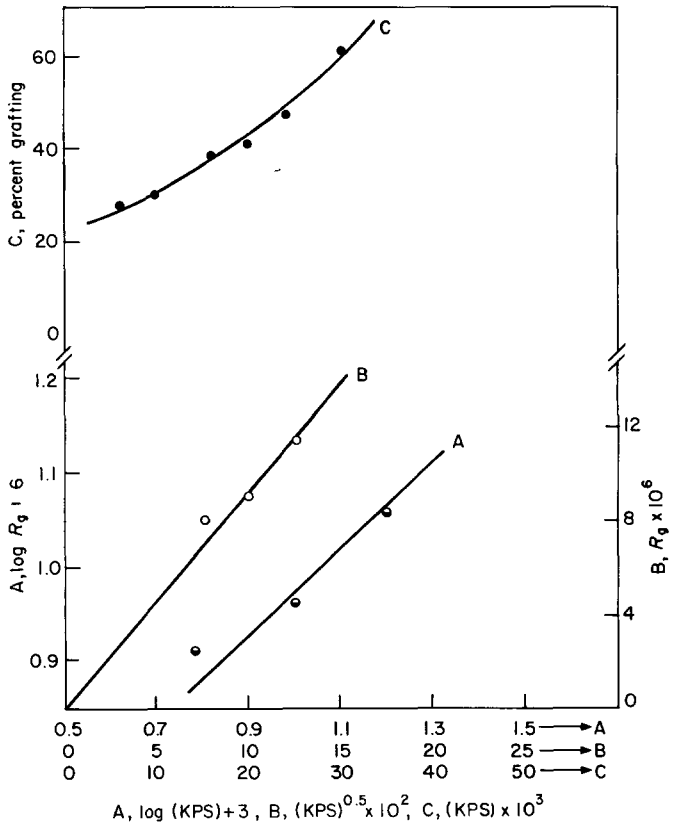

Figure 2 Effect of [initiator] on grafting: A, log R_g *versus* log[KPS]; B, R_g *versus* $[KPS]^{0.5}$; C, percent grafting *versus* [KPS]

CHARACTERIZATION

Amino acid analysis of graft copolymers

Graft copolymers were hydrolysed using 6N hydrochloric acid for 22 h at 110°C and evaporated under vacuum at 40°C–50°C. The residue was dissolved in sodium citrate buffer at pH 2.2 and then analysed.

A comparison of the amino acid composition of the grafted and ungrafted gelatins showed a significant decrease in serine, histidine, tyrosine, lysine and threonine. These results, therefore, indicate that these groups may be involved as the grafting sites. It is not clear whether the increase in proline and glycine content is caused by transformation of other amino acids by the action of an oxidizing agent used in the present study. That proline and hydroxyproline residues in proteins are susceptible to oxidation has been demonstrated by earlier workers[9,10].

The primary $SO_4^{\bullet}$ radicals produced would initiate the graft copolymerization reaction. Furthermore, these primary radicals may form a redox system with some reducing sites in gelatin to form free radicals on the backbone itself. Similar results have been obtained by Sakurada *et al.*[11].

Mechanism and rate law

From the above discussions it is observed that the rate of grafting (R_g) is proportional to the one and half power of the monomer, the half power of the initiator and the half power of the backbone concentration. The above

Table 4 Effect of [gelatin] on grafting

$[Gelatin] \times 10^4$ (mol l^{-1})	$R_g \times 10^6$ (mol l^{-1} s^{-1})	Grafting efficiency	Percent grafting
2.2	7.00	80.64	18.52
2.5	8.12	83.58	21.58
3.2	10.43	85.20	25.62
3.8	11.92	87.39	29.47
4.8	10.66	86.52	22.24
6.3	7.64	84.46	19.62

$[BA] = 1.4 \times 10^{-1}$ mol l^{-1}
$[KPS] = 10 \times 10^{-3}$ mol l^{-1}
Total volume = 50 ml
Temperature = 60°CTime = 90 min

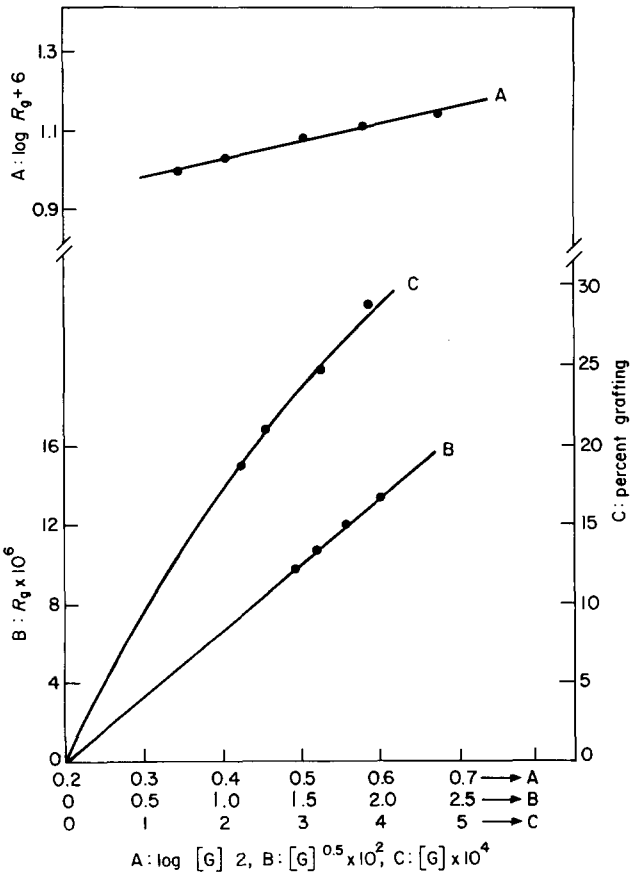

Figure 3 Effect of [gelatin] on grafting: A, log R_g *versus* log[gelatin]; B, R_g *versus* [gelatin]; C, percent grafting *versus* [gelatin]

Table 5 Effect of temperature on grafting

Temperature °C	$R_g \times 10^6$ (mol l^{-1} s^{-1})	Grafting efficiency	Percent grafting
30	1.74	30.10	5.20
40	2.79	48.21	9.35
50	10.16	64.13	15.33
60	15.33	72.45	26.65
70	10.21	60.31	24.05
80	4.40	51.20	14.67

$[BA] = 1.4 \times 10^{-1}$ mol l^{-1}
$[KPS] = 10 \times 10^{-3}$ mol l^{-1}
$[Gelatin] = 3.3 \times 10^{-4}$ mol l^{-1}
Total volume = 50 ml
Time = 90 min

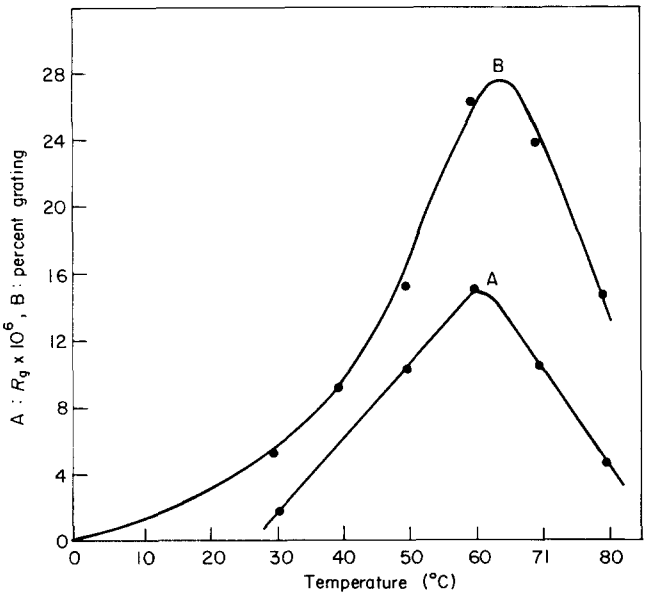

Figure 4 Effect of temperature of grafting: A, R_g *versus* temperature (°C); B, percent grafting *versus* temperature (°C)

observations may lead to the following mechanism for the graft copolymerization reaction.

(1) Production of gelatin radicals [G•]

$$G + I \xrightarrow[k]{K} \text{complex} \quad (1)$$

$$\text{complex} + M \xrightarrow{k_1} G^\bullet + M^\bullet + \text{products} \quad (2)$$

(2) Initiation with monomer

$$G^\bullet + M \xrightarrow{k_2} GM^\bullet \quad (3)$$

(3)Propagation

$$GM^\bullet + M \xrightarrow{k_p} GM_2^\bullet \quad (4)$$

$$GM_{n-1}^\bullet + M \xrightarrow{k_p} GM_n^\bullet \quad (5)$$

$$M^\bullet + M \xrightarrow{k_p} M_n^\bullet \quad (6)$$

(4) Radical recombination

$$2GM_n^\bullet \xrightarrow{k_t} \text{non radical products} \quad (7)$$

$$M_n^\bullet + M_n^\bullet \xrightarrow{k_t} \text{non radical products} \quad (8)$$

(5) Rate law: assuming steady state conditions

$$Kk_1[G][I][M] = k_2[G^\bullet][M] \quad (9)$$

$$[G^\bullet] = \frac{Kk_1[G][I]}{k_2} \quad (10)$$

$$k_2[G^\bullet][M] = k_t[GM_n^\bullet]^2 \quad (11)$$

$$[GM_n^\bullet]^2 = \frac{k_2[G^\bullet][M]}{k_t} \quad (12)$$

$$[GM_n^\bullet] = \frac{k_2^{1/2}[G^\bullet]^{1/2}[M]^{1/2}}{k_t^{1/2}} \quad (13)$$

$$R_g = k_p[GM_n^\bullet][M] \quad (14)$$

substituting equation (13) for [GM•] in equation (14)

$$R_g = \frac{k_p K^{1/2} k_1^{1/2}[G]^{1/2}[I]^{1/2}[M]^{3/2}}{k_t^{1/2}} \quad (15)$$

or

$$R_g = k_g[G]^{1/2}[I]^{1/2}[M]^{3/2} \quad (16)$$

where

$$k_g = \frac{k_p K^{1/2} k_1^{1/2}}{k_t^{1/2}} \quad (17)$$

Table 6 Amino acid composition of gelatin and gelatin graft copolymers

Amino acids	Control	Sample I	Sample II
Hydroxyproline	103.7	150.2	160.0
Aspartic acid	50.7	41.2	47.6
Threonine	14.0	10.2	12.2
Serine	36.2	21.2	18.3
Glutanic acid	73.5	68.2	63.2
Proline	150.3	200.1	195.4
Glycine	335.0	333.1	330.5
Alanine	100.3	74.5	76.2
Valine	17.7	17.2	16.1
Methionine	0.5	–	–
Isoleucine	12.6	12.2	10.6
Leucine	21.0	18.2	16.0
Tyrosine	1.2	0.9	0.9
Phenylalanine	9.7	8.5	8.0
Hydroxylsine	6.8	5.0	5.8
Lysine	23.9	15.5	10.4
Histidine	3.4	1.2	1.0
Arginine	40.0	32.1	28.2
	1000.5	999.5	1000.7

Values are expressed as residues per 1000 total residues

Conditions	Sample I	Sample II
Reaction time	90 min	90 min
Temperature	60°C	60°C
Gelatin	3.2×10^{-2} mol l^{-1}	3.2×10^{-2} mol l^{-1}
[KPS]	10×10^{-3} mol l^{-1}	10×10^{-3} mol l^{-1}
Amount of monomer	1 ml	2 ml

where $G^{\bullet}$, $GM_n^{\bullet}$, $M^{\bullet}$ and $I^{\bullet}$ refer to gelatin radical, gelatin graft radical, monomer radical and initiator radical respectively.

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