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GLUTARALDEHYDE CROSSLINKED GELATIN WITH POLYACRYLAMIDE GRAFTS*

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ABSTRACT

Persulfate-initiated grafting of crosslinked gelatin with acrylamide in aqueous medium is investigated. The high percentages of grafting are explained as a direct consequence of the heterophase nature of grafting. Optimum reaction conditions for a high percentage of grafting together with low homopoymer yields are discussed.

INTRODUCTION

Crosslinked gelatin is an adaptable matrix which can anchor hydrophilic or hydrophobic grafts [1]. When gelatin is crosslinked, it is insoluble in water but can still swell to some extent [2]. On the other hand, the graft copolymers can swell extensively in appropriate solvents. Crosslinked gelatin with polyacrylamide grafts has interesting features; it can swell extensively in water, and the contiguous amide groups can be effective chelating ligands. The combination of these two properties has wide ranging implications for this material in controlled release technology [3].

This paper examines the persulfate-initiated grafting of crosslinked gelatin with acrylamide in aqueous medium. Graft copolymers of soluble gelatin have been widely explored [1, 4–8]. In an earlier report [1] we discussed the preparation and properties of the graft copolymers of gelatin with polyacrylic acid, poly(methyl acrylate), and poly(methyl methacrylate). In these studies the grafting preceded the crosslinking step. The gelatin–persulfate–aqueous acrylic acid was a homo-

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geneous system. The gelatin–persulfate–methyl acrylate/methyl methacrylate resembled a suspension polymerization system. In the present system, except for Gelx and Gelx-*g*-PAam, the reactants and products are water soluble. Thus, while the homopolymerization follows general solution kinetics, grafting occurs under heterogeneous conditions. With the progress of the reaction, the viscosity of the medium steadily rises and inevitably leads to gelling due to increased homopolymer yields [9]. Quantitative separation of the product becomes cumbersome. A careful look at the grafting time, monomer concentration, initiator concentration, and dilution effects with respect to percentage grafting and grafting efficiency is necessary to solve this problem. We present here the results of such an investigation.

EXPERIMENTAL

Bacteriological gelatin, acrylamide, and glutaraldehyde (25% aqueous solution) were supplied by Loba Chemicals, Bombay. Potassium persulfate (BDH) and A.R. Grade solvents were used as such. All reactions were carried out in oxygen-free distilled water.

The following abbreviations will be used throughout:

Crosslinked gelatin:	Gelx
Acrylamide:	Aam
Polyacrylamide:	PAam
Potassium persulfate:	KPS
Crosslinked gelatin with polyacrylamide grafts:	Gelx-*g*-PAam

Preparation of Gelx

Gelatin was crosslinked using 4% aqueous glutaraldehyde as described earlier [1, 2]. The crisp granules were washed thoroughly with water and later with acetone. The sample was subsequently dried under vacuum at 40° C.

Preparation of Gelx-*g*-PAam

Reaction flasks with specified quantities of Gelx, acrylamide, KPS, and water were kept in a thermostat shaker maintained at the requisite temperature to ensure uniform conditions. To end the reaction, hydroquinone was first added as the quencher and then the reaction mixture was extracted exhaustively with water to remove the homopolymer. The Gelx-*g*-PAam was dried under vacuum and weighed. The percentage grafting and grafting efficiences were calculated as follows:

$$\text{Percentage grafting} = \frac{\text{wt of grafted PAam}}{\text{wt of Gelx}} \times 100$$

$$\text{Efficiency of grafting} = \frac{\text{wt of PAam grafted}}{(\text{wt of PAam grafted}) + (\text{wt of PAam homopolymer})}$$

Swelling Studies

The swelling behavior of Gelx in aqueous solutions of KPS and Aam was monitored gravimetrically under the conditions used for grafting (65°C, 2 h). The extent of swelling was evaluated against swelling in pure double distilled water taken as 100%.

$$\text{Percent swelling} = \frac{\text{swelling in medium}}{\text{swelling in pure water}} \times 100$$

RESULTS AND DISCUSSIONS

Moderately swollen Gelx granules in which the monomer and the initiator are present in relatively high abundance provide a conducive environment for the initiation and propagation of graft copolymerization. This situation can lead to an unusually high percentage of grafting, characteristic of heterophase polymerizations [9]. The results substantiate this assumption.

Grafting Time–The Induction Period

The dependence of percentage grafting and grafting efficiency on duration of grafting is given in Fig. 1. It appears that the creation of active centers on the Gelx is slow and random. In all probability, the initiation of homopolymerization is more efficient than the creation of grafting sites on Gelx. This could account for the induction period. Kojiyama et al. [10] reported low initial graftings for the collagen–methyl methacrylate–tributyl tin system. However, once the sites are created, propagation of the grafted chain becomes equally competitive or perhaps even more efficient due to microdomains of higher activity within the swollen Gelx granules. Longer reaction times do not seem to favor a higher percentage of grafting. The rapid depletion of the monomer and the increasing viscosity of the medium might be responsible for this [10].

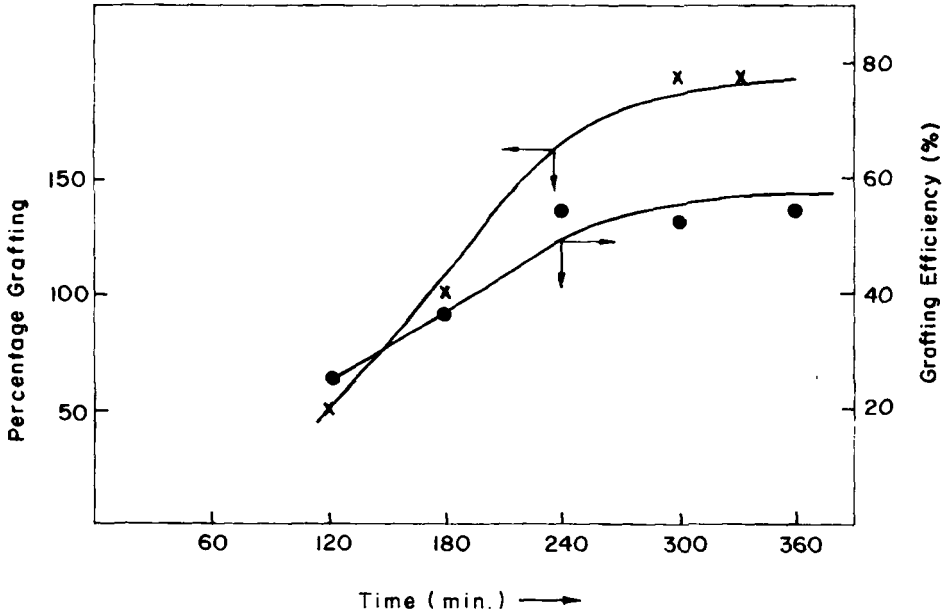

FIG. 1. Effect of time on percentage grafting (×) and grafting efficiency (●). Gelx = 1 g, Aam = 70 mmol, KPS = 9.25 mmol/L, total volume = 20 mL, 65°C.

The Initiator Concentration

Figure 2 shows the optimum concentration of KPS to be 7.5×10^{-3} mol/L. George et al. [5-7] investigated the KPS–acrylonitrile ethyl acrylate–gelatin system and observed a similar behavior. We felt that increasing concentrations of KPS would hinder the swellability of Gelx, consequently decreasing grafting. To substantiate this, we monitored the swelling profile of Gelx in aqueous solutions of KPS and acrylamide. The results were in agreement with our assumption. It is relevant to cite the studies of Gringnon et al. [11] on the swelling behavior of carboxymethyl cellulose. They found that the water retention capacity of carboxymethyl cellulose in 1% NaCl was a fraction of that for water.

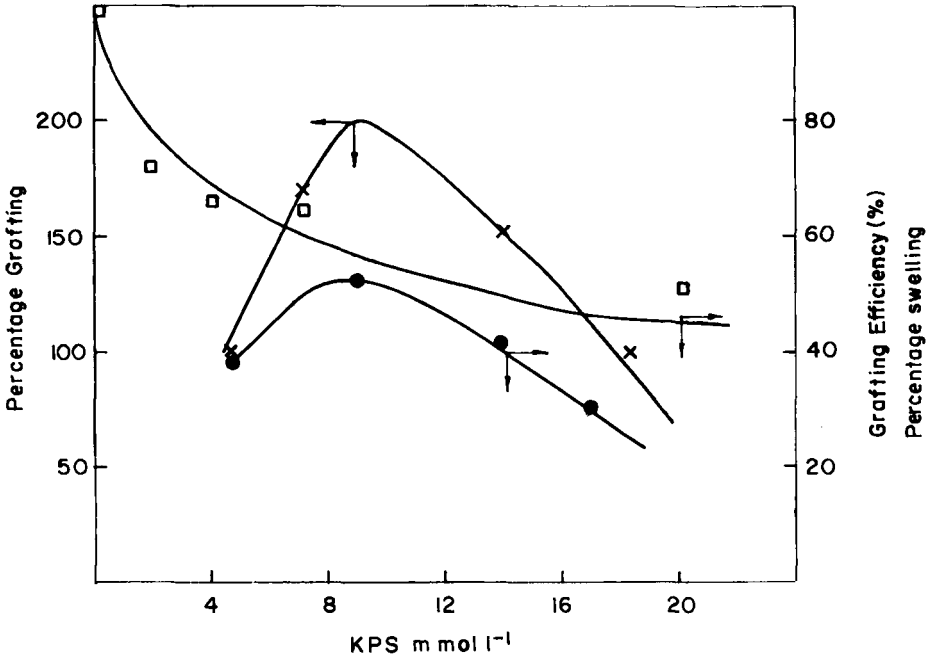

FIG. 2. Effect of KPS concentration on (×) percentage grafting, (●) grafting efficiency, and (○) swelling profile of Gelx in aqueous KPS. For grafting experiments, Gelx = 1 g, Aam = 70 mmol, aqueous phase = 20 mL, 65°C.

The Acrylamide:Gelx Ratio

Percentage grafting and grafting efficiency as a function of acrylamide to Gelx ratio (A/G values) were monitored, rather than a simple variation in acrylamide concentration. The results show that the percentage grafting falls off at high A/G values (Fig. 3).

At an A/G value of 2.5, very little homopolymer (5%) is formed; at a value of 5 the homopolymer yield increases (10–20%) but it is still reasonable enough to effectively separate the homo and graft copolymers. At still higher values of A/G, the homopolymerization is overwhelmingly high.

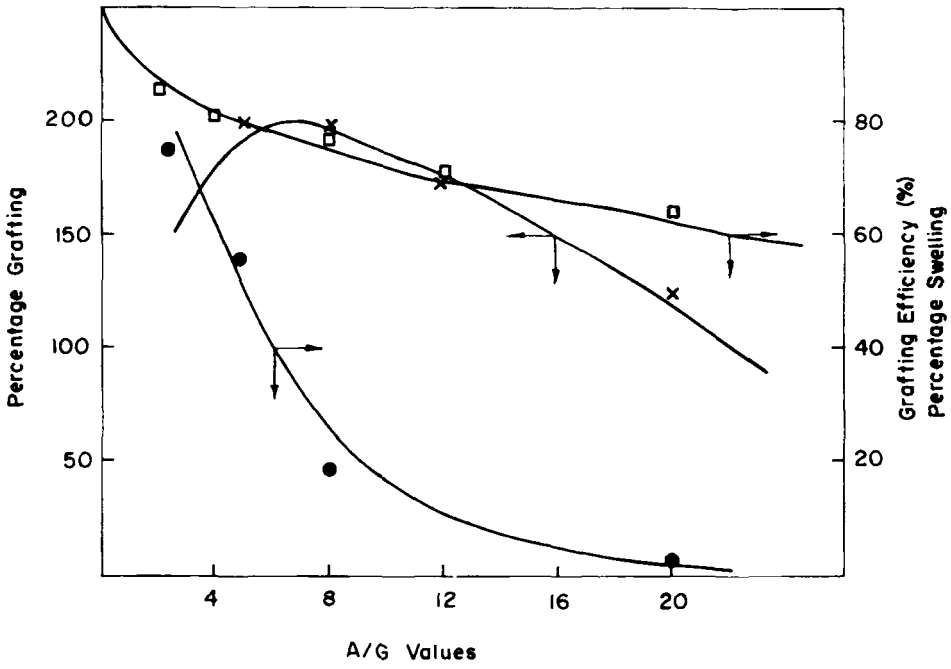

FIG. 3. Influence of A/G values (acrylamide to Gelx ratio, g/g) on (×) percentage grafting, (●) grafting efficiency, and (□) swelling characteristics of Gelx in aqueous Aam solutions. For grafting experiments, Gelx = 1 g, KPS = 9.25 mmol/L, total volume = 20 mL, 65°C.

As far as the grafting is concerned, it is possible that increased concentrations of monomer acrylamide in the medium might impose limiting conditions on the swelling characteristics of Gelx, as shown in Fig. 3. This could lead to a preponderance of homopolymerization.

The Dilution Effect

Since gelling is the main constraint in Gelx-*g*-PAam synthesis, the liquor-to-material ratio acquires great significance. The dilution effects were evaluated by varying the volume of the aqueous phase with respect to the total solid content. Very low and very large volumes were found to be unfavorable for grafting (Fig. 4). At low volumes the effective density of the system will be high, which might suppress the tendency of Gelx granules to swell. On the other hand, at high dilutions the effective concentration of the monomer/initiator will be so low that the percentage grafting invariably falls.

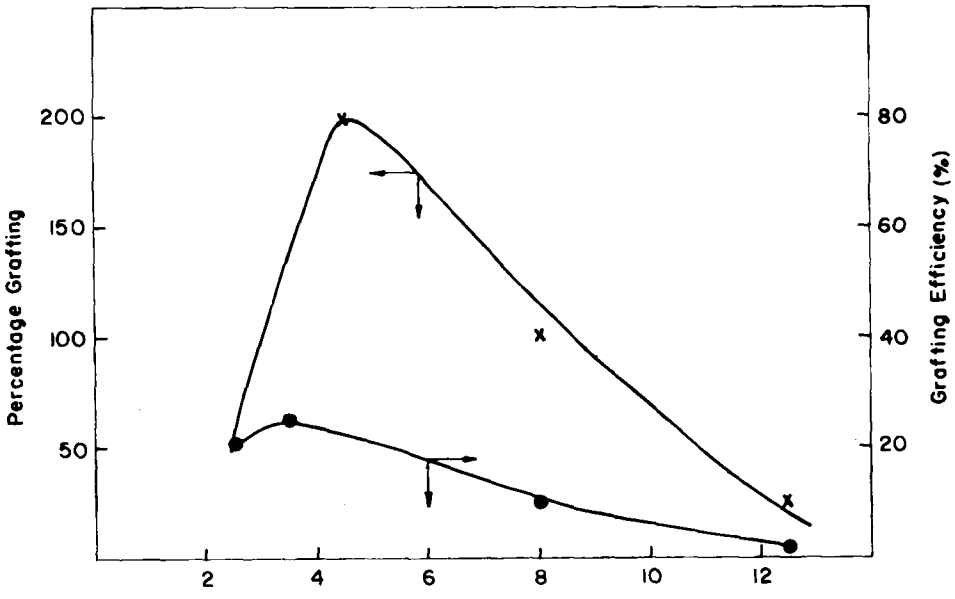

FIG. 4. Influence of liquor to material ratio values (the abscissa) on (×) percentage grafting and (●) efficiency of grafting. Gelx = 1 g, Aam = 5 g, KPS = 9.25 mmol/L, 65°C.

Mechanism of Grafting

It has been proposed [12, 13] that creation of free radical centers on gelatin involves hydrogen abstraction, and that the propagation and termination steps follow their normal course. The same mechanism could also be operating in the Gelx–Aam–KPS system. This can be represented as

$$\underset{[I_2]}{S_2O_8^{2-}} \xrightarrow{\text{decomposition}} \underset{(2I^{\cdot})}{2SO_4^{-\cdot}} \qquad (1)$$

$$I + Gelx \xrightarrow{\text{H abstraction}} I\text{-}H + Gelx \qquad (2)$$

We compared the amino acid analysis data of Gelx and Gelx-*g*-PAam to locate the

grafting sites. The results (data not shown) showed the grafting sites on Gelx to be totally random, with no preference for hydrogen abstraction from any particular residue.

CONCLUSIONS

Gelx swells modestly in an aqueous polymerization medium and creates a favorable environment for the initiation and propagation of grafting. Grafted polyacrylamide chains enhance the swellability of Gelx-*g*-PAam, and grafting becomes more efficient. However limitations are soon reached. This is because the swellabilities of both Gelx and Gelx-*g*-PAam are direct functions of the osmotic pressure differential and viscosity of the aqueous phase. This explains why the percentage grafting passes through a maximum with respect to the monomer and initiator concentrations.

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