# NOTES

## *Grafting of Ethyl Acrylate onto Gelatin*

### INTRODUCTION

Graft copolymerization permits tailor-making of the polymer structure so that branches may be entirely different from the backbone. The major justification for utilizing graft copolymer is that this type of hybrid is a single chemical species that displays the properties characteristic of each of the components rather than an averaging of their properties.

Even though grafting of synthetic polymers onto gelatin has been reported earlier,[1-5] much of this work is in the form of patent publications which are written to support claims rather than to explain the chemistry involved. The addition of monomers to gelatin was found to be similar to vinyl polymerization to give an extended carbon atom chain attached to the side group of the gelatin molecule. The length of the side chain polymer graft formed is dependent upon the reaction conditions. In the present investigation ethyl acrylate was grafted onto gelatin using potassium persulfate as the initiator in aqueous medium. Of all solvents, water is unique in being a poor chain transfer agent,[6] a property which often introduces quite novel and unexpected features. The grafting reactions were conducted at 60°C in preference to low temperatures to facilitate high grafting yields. Investigations were carried out to study the effects of variation in (i) reaction time, (ii) concentration of monomer, (iii) concentration of initiator, (iv) concentration of backbone, and (v) temperature on the rate of grafting.

### EXPERIMENTAL METHODS

**Materials.** Gelatin (Riedel, Germany) was used as such in this investigation. Monomer ethyl acrylate (Koch Light Laboratories, Ltd., England) was purified as reported earlier.[7] Initiator used was potassium persulfate (KPS) (Riedel, Germany).

**Graft Copolymer Procedure.** A 10% solution of gelatin was prepared in warm water and used in graft copolymerization. Fresh solution of gelatin was prepared for the experiment to avoid bacterial growth. Requisite amounts of monomer, initiator, and gelatin solution were added. Deaeration with nitrogen was continued throughout the course of reaction as this ensured not only an inert atmosphere but also continuous stirring. The tube was then thermostated at 60 ± 0.1°C. After specific polymerization time (90 min) the reaction tube was immersed in a freezing mixture to arrest the reaction. The contents was then poured into ice cold methanol. The polymer suspension are then filtered in weighed sintered glass crucibles and dried in vacuum at 40–50°C overnight to a constant weight.

**Isolation of the Graft Copolymer.** The gross polymer obtained in the present case consists of unreacted gelatin, graft copolymer, and unbound homopolymer. These are separated by the Soxhlet extraction method. The unbound homopolymer was completely extracted with acetone.

The value of the rate of total monomer conversion was calculated gravimetrically. The rate of graft copolymerization ($R_g$) and the grafting efficiency (GE) were calculated from the following expressions:

$$R_g = R_p - R_h$$

$$\text{GE} = \frac{R_g}{R_p} \times 100 = \frac{R_g}{(R_g + R_h)} \times 100$$

### RESULTS AND DISCUSSION

**Effect of Reaction Time.** The grafting of EA onto gelatin was studied as a function of time and the results are given in Figure 1. With the increase in grafting reaction time, percent grafting, grafting efficiency, and rate of grafting were found to be increased. At the initial stages the rate of grafting increased slowly and then leveled off after 90 min. Longer reaction periods have little effect on the degree of grafting. This may be due to the fact that the primary radicals produced in the initial stages might have been utilized in activating the backbone and no more new active sites have been created on the backbone. Similar results were also reported by other investigators.[7,8]

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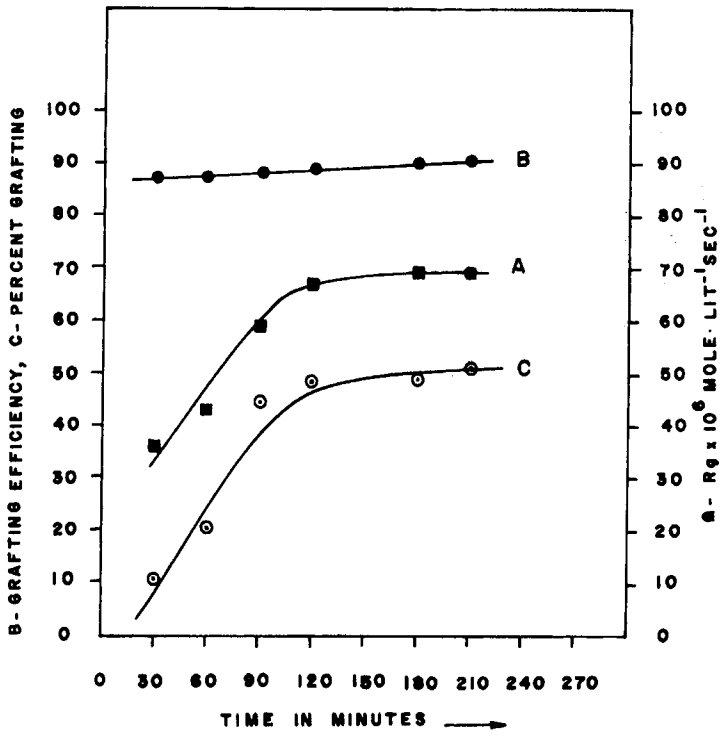


Fig. 1. Effect of time on grafting: (A) $R_g$ vs. time; (B) grafting efficiency vs. time; (C) percent grafting vs. time.

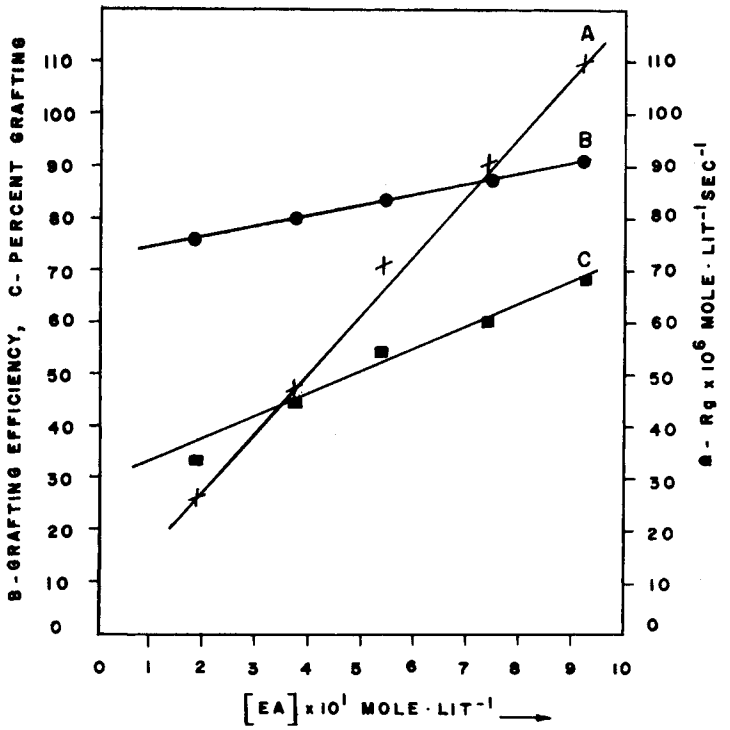


Fig. 2. Effect of [monomer] on grafting: (A) $R_g$ vs. [EA]; (B) grafting efficiency vs. [EA]; (C) percent grafting vs. [EA].

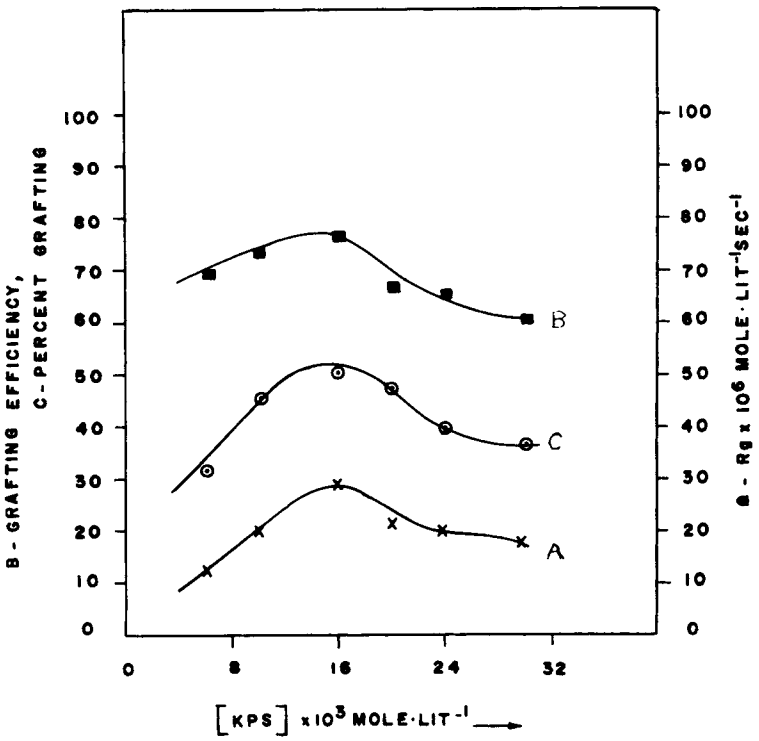


Fig. 3. Effect of [initiator] on grafting: (A) $R_g$ vs. [KPS]; (B) grafting efficiency vs. [KPS]; (C) percent grafting vs. [KPS].

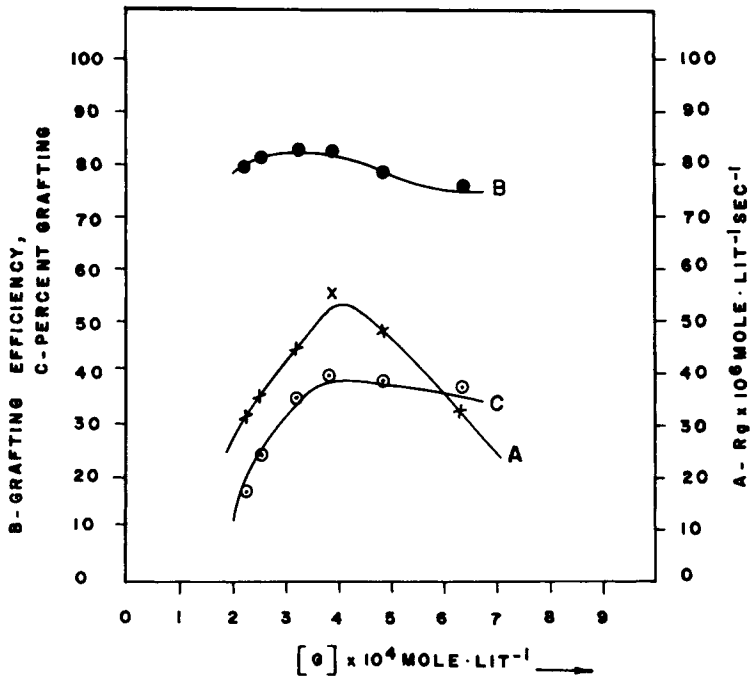


Fig. 4. Effect of [gelatin] on grafting: (A) $R_g$ vs. [G]; (B) grafting efficiency vs. [G]; (C) percent grafting vs. [G].

TABLE I
Effect of Temperature on Grafting[a]

| Temp (°C) | $R_g \times 10^6$ mol·L$^{-1}$·s$^{-1}$ | Grafting efficiency | Percent grafting |
|---|---|---|---|
| 30 | 11.54 | 91.33 | 20.10 |
| 40 | 20.51 | 90.90 | 37.39 |
| 50 | 25.10 | 88.42 | 41.24 |
| 60 | 34.07 | 81.28 | 50.24 |
| 70 | 32.77 | 80.00 | 46.10 |
| 80 | 29.28 | 76.24 | 31.20 |

[a] [EA] = $1.8 \times 10^{-1}$ 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.

**Effect of Monomer Concentration.** There is a regular increase in percent grafting, grafting efficiency, and rate of grafting with increase in monomer concentration (Fig. 2). Increase in rate of grafting observed upon increasing the monomer concentrations is probably due to gel effect which arises when the polymerizing medium becomes highly viscous. This increase in viscosity was found to have reduced the termination state of the growing chains due to the slower diffusion which in turn leads to higher molecular weights and higher rates of grafting and grafting efficiency. This is in conformity with the results obtained in grafting of poly(ethyl acrylate) onto wool.[9] Chain lengths of the grafts were found to increase with increase in monomer concentration.

**Effect of Initiator Concentration.** Potassium persulfate was found to be an efficient initiator for grafting of vinyl monomers onto gelatin. In the present investigation the initiator concentration was varied from $6.0 \times 10^{-3}$ mol·L$^{-1}$ to $3.0 \times 10^{-2}$ mol·L$^{-1}$. It is seen that percent grafting, grafting efficiency, and the rate of grafting increases up to critical initiator concentrations of $1.6 \times 10^{-2}$ mol·L$^{-1}$ and then decreases (Fig. 3).

As gelatin and potassium persulfate are soluble in aqueous medium, the approach of initiating radicals to gelatin is facilitated, which may result in an interaction with the functional group of gelatin to produce gelatin radicals. Further primary radicals may also form a redox system on the backbone itself as in the case of potassium persulfate initiated grafting of poly(methyl methacrylate) onto poly(vinyl alcohol),[10] thus resulting in an initial increase in percent grafting values. When the initiator concentration is progressively increased, the side chain termination takes place even before its full growth. This is because of the fact that higher initiator concentrations yield a greater number of primary radicals, gelatin radicals, and growing macroradicals of side chains which may interact with each other, resulting in termination, thus reducing chain length, grafting efficiency, and percent grafting.

**Effect of Backbone Concentration.** The variation of gelatin concentration has a profound effect on percent grafting, grafting efficiency, and rate of grafting as seen in Figure 4.

Percent grafting and grafting efficiency increased initially with increase in gelatin concentration, then reached a maximum value, and finally decreased with further increase in gelatin concentration. The initial increase may be due to the fact that the reactive sites increase with increase in the concentration of gelatin. The decrease is due to destruction of radical activity on the backbone soon after it is formed due to termination between backbone–backbone and backbone–primary radicals. This is in agreement with the results obtained in the grafting of acrylonitrile onto starch[11] and grafting of methyl acrylate onto gelatin.[12]

**Effect of Temperature.** An optimum temperature is required for maximum grafting as seen in Table I. Percent grafting and rate of grafting increases up to 60°C, after which the value decreases. This may be due to any one or the combination of all the effects given below: (a) coagulation of polymer at higher temperatures; (b) decomposition of KPS at higher temperatures liberating oxygen; (c) degradation of gelatin at higher temperatures. Similar optimum temperature for maximum grafting was required in the graft copolymerization onto wool.[13]

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