

Grafting of Glycidyl Methacrylate onto Gelatin

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SYNOPSIS

Gelatin was graft copolymerized with poly(glycidyl methacrylate) using potassium peroxydisulfate in aqueous medium. Effect of temperature, time, initiator, monomer, and backbone concentrations were studied. The percent grafting was found to increase initially and then decrease in all the cases except with variation of monomer concentration. The rate of grafting, grafting efficiency, and percent of grafting were calculated. The grafting results have been discussed in the light of the rate of grafting. Mechanical properties, FT IR spectra, percent swelling, and percent dye uptake were carried out on the graft copolymerization and the results discussed.

INTRODUCTION

Gelatin is one of the most versatile natural products known. The number and the variety of reactive groups along the chain open up the field to a very long list of potential reagents. Addition of monomers¹⁻⁴ to gelatin was found to be similar to vinyl polymerization to give an extended carbon chain attached to the side group of the gelatin molecules. The length of the side chain polymer graft formed is dependent on the reaction conditions.

Grafting of gelatin by various polymers has been studied with the objective of improving or modifying the properties of gelatin and in order to develop new materials combining the desirable properties of both natural and synthetic polymers.^{4,5} Gelatin both in native and modified form has been used for various applications.⁶⁻⁹ Proteins like gelatin,^{10,11} casein,^{12,13} collagen,¹⁴ wool,¹⁵ silk,¹⁶ and other polymers such as starch^{17,18} or cellulose¹⁹ are modified by grafting various polymers onto them.

Peroxydisulfate was found to be the most efficient initiator. Hydrophobic interactions in the binding of the Rosebengal dye onto the poly(vinyl pyrrolidone) has been reported.²⁰ We have chosen amphipathic substrate like Rosebengal with ionic and hydrophilic groups.

The dye has electrostatic binding sites and hydrophilicity. Stejskal et al.²¹ characterized, at the molecular level, gelatin grafted by PMMA by light scattering.

EXPERIMENTAL

Materials

Gelatin $\bar{M}_w = 60,000$ (Sigma Chemical Co.) and potassium peroxydisulfate (Merck, Germany) were used as such without further purification. Monomer, glycidyl methacrylate (GMA) (Fluka AG) was purified by distillation under vacuum. The middle fraction was used in the experiment.

Grafting Procedure

A known amount of gelatin was dispersed in water at constant stirring under nitrogen atmosphere and maintained at the required temperature. After sufficient time glycidyl methacrylate was added followed by the initiator, potassium peroxydisulfate. After the completion of the reaction, the contents were poured in methanol and the precipitated products were filtered and dried.

The dried products were Soxhlet extracted for removal of unbound homopolymer using acetone as solvent and dried in vacuum to constant weight. It was, however, observed that the poly(GMA) pre-

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pared under similar conditions was only partially soluble in acetone probably indicating the cross-linking through epoxide group.

CHARACTERIZATION

Mechanical Studies

Mechanical studies of the gelatin-grafted films were measured using Instron Universal Testing Machine (Model 1112).

Dye Uptake Studies

The dye uptake studies of gelatin-grafted products were carried out with Shimadzu, UV-260 spectrophotometer.

Swelling Studies

Swelling studies of the grafted products were done in water.

FT IR Spectra

Pure gelatin and grafted gelatin films were characterized by FT IR analysis for the proof of grafting using the NICOLET 20-DXB FTIR spectrophotometer.

CALCULATIONS

The percent grafting (PG), graft efficiency (GE), and rate of grafting (R_g) were calculated as follows:

$$1. \text{ Percent grafting (PG)} = \frac{\text{weight of graft copolymer} - \text{weight of gelatin}}{\text{weight of gelatin}} \times 100$$

$$2. \text{ Grafting efficiency (GE)} = \frac{\text{weight of grafted polymers}}{\text{weight of grafted polymers} + \text{weight of unbound homopolymer}} \times 100$$

$$3. \text{ Rate of grafting (} R_g \text{)} = R_p - R_h, \text{ where } R_p \text{ is the total rate of polymerization and } R_h \text{ is the rate of homopolymerization.}$$

Tensile strength and percent of elongation, percent of dye uptake, and percent swelling were calculated as follows:

$$4. \text{ Tensile strength} = \frac{\text{breaking load (} K_g \text{)}}{\text{cross section area (cm}^2 \text{)}}$$

$$5. \text{ Percent elongation} = \frac{\text{length in chart (cm)}}{\text{original length (cm)}} \times \frac{100}{\text{magnification ratio}}$$

where magnification ratio = chart speed (cm/min)/cross head speed (cm/min)

$$6. \text{ Percent of dye uptake} = \frac{\text{OD(I)} - \text{OD(II)}}{\text{OD(I)}} \times 100$$

where OD(I) is the optical density of the dye solution and OD(II) is the optical density after immersing the grafted polymer in the dye solution.

$$7. \text{ Percent swelling} = \frac{\text{swollen sample weight} - \text{initial weight}}{\text{initial weight}} \times 100$$

RESULTS AND DISCUSSION

The influence of concentration of backbone, monomer initiator, and the effect of temperature and time on the graft copolymerization of glycidyl methacrylate onto gelatin were investigated and the results are discussed.

Effect of Backbone Concentration

The dependence of the grafting on the concentration of gelatin was studied in the range of $6.6\text{--}11 \times 10^{-4}$ mol/L and the results are depicted in Table I. Percent grafting and grafting efficiency increased initially with increase in gelatin concentrations, reached a maximum value, and finally decreased with further increase in gelatin concentration. These results are also obtained in the grafting of acrylonitrile onto starch,²² and grafting of acrylonitrile onto gelatin.¹⁰ The initial increase may be due to the fact that the reactive sites increased with increase in the concentration of gelatin. The decrease is due to the destruction of radical activity on the backbone because of the increase in the viscosity.

Effect of Monomer Concentration

There is regular increase in percent grafting, grafting efficiency, and rate of grafting with increase in monomer concentration (Table II). Increase in rate of grafting observed upon increasing the monomer concentration is probably due to the gel effect that arises when polymerizing medium becomes highly viscous. This increase in viscosity was found to have reduced termination rate of the growing chains, due to their slower diffusion, which in turn leads to higher rates of grafting and grafting efficiency.

Table I Effect of Gelatin Concentration on Grafting^a

[Gelatin] $\times 10^4$ mol/L	$R_g \times 10^6$ mol/L s ⁻¹	Grafting Efficiency	Percent Grafting
6.60	31.15	86.90	43.0
8.33	53.44	92.50	58.8
10.00	121.84	92.61	95.0
11.00	54.57	92.53	47.0

^a [KPS] = 1.83×10^{-3} mol/L; [GMA] = 6.8×10^{-1} mol/L; total volume = 100 mL; temperature = 50°C; time = 120 min.

Table II Effect of GMA Concentration on Grafting^a

[GMA] $\times 10$ mol/L	$R_g \times 10^6$ mol/L s ⁻¹	Grafting Efficiency	Percent Grafting
4.1	26.78	90.59	33.4
5.4	38.24	91.00	42.4
6.80	53.44	92.50	58.8
8.2	78.64	91.18	86.8
9.6	111.65	97.44	131.2

^a [KPS] = 1.83×10^{-3} mol/L; [Gelatin] = 8.3×10^{-4} mol/L; total volume = 100 mL; temperature = 50°C; time = 120 min.

Effect of Initiator Concentration

In the present investigation concentration was varied from 1.85×10^{-3} to 3.33×10^{-3} mol/L. It is observed that percent grafting, grafting efficiency, and rate of grafting increase up to a critical initiator concentration of 2.96×10^{-3} mol/L and then decreased (Table III) as in the case of potassium peroxydisulfate initiated grafting of poly (MMA) onto to poly (vinyl alcohol).²³ This is because higher initiator concentrations yield a greater number of primary radicals, gelatin radicals, and growing macro radicals of side chains, which may interact with each other resulting in termination, thus reducing grafting efficiency and percent grafting.

Effect of Temperature

An optimum temperature required for maximum grafting, as in (Table IV), was 50°C. Percent grafting increased up to 60°C, after which the values decreased because of coagulation of polymer at high

Table III Effect of Peroxydisulphate Concentration on Grafting^a

[KPS] $\times 10^3$ mol/L	$R_g \times 10^6$ mol/L s ⁻¹	Grafting Efficiency	Percent Grafting
1.85	55.44	92.65	58.8
2.59	76.64	97.27	84.0
2.96	94.22	96.60	103.2
3.33	90.73	93.90	99.3

^a [GMA] = 6.8×10^{-1} mol/L; [Gelatin] = 8.3×10^{-4} mol/L; total volume = 100 mL; temperature = 50°C; time = 120 min.

Table IV Effect of Temperature on Grafting^a

Temperature (°C)	Percent Grafting
50	58.8
60	141.0
70	115.0
80	112.0

^a [GMA] = 6.8×10^{-1} mol/L; [Gelatin] = 8.3×10^{-4} mol/L; [KPS] = 1.83×10^{-3} mol/L; total volume = 100 mL; time = 120 min.

temperature, decomposition of peroxydisulfate liberating oxygen, and degradation of gelatin at higher temperatures. Similar optimum temperature has been reported for maximum grafting required in the copolymerization onto gelatin.²⁴

Effect of Time

The grafting of GMA onto gelatin was studied as a function of time, and the results are given in Table V. With the increase in the grafting reaction time, percent grafting increased up to 240 min and then decreased with further increase in time because of degradation of gelatin.

CHARACTERIZATION STUDIES

Mechanical Properties

In the present investigation the physical properties were determined for modified gelatin, namely, (i)

Table V Effect of Time on Grafting^a

Time (min)	Percent (Grafting)
120	58.8
180	64.0
240	128.0
300	72.6
420	66.0

^a [GMA] = 6.8×10^{-1} mol/L; [Gelatin] = 8.3×10^{-4} mol/L; [KPS] = 1.83×10^{-3} mol/L; total volume = 100 mL; temperature = 50°C.

Table VI Effect of [GMA] Variation on Percent Grafting versus Tensile Strength and Percent Elongation

[GMA] × 10 mol/L	Percent Grafting	Tensile Strength (kg/cm ²)	Percent Elongation
4.1	33.4	139.0	106.05
5.4	42.4	150.1	34.09
8.2	86.8	165.0	20.64
9.6	131.2	175.4	15.15

^a [KPS] = 1.83×10^{-3} mol/L; [Gelatin] = 8.3×10^{-4} mol/L; total volume = 100 mL; temperature = 50°C; time = 120 min.

the tensile strength and (ii) percent elongation. The tensile strength and percent elongation in the graft copolymer films vary with percent of grafting. It may be seen that an increased percent of grafting increases the tensile strength and decreases the percent elongation (Table VI), which may be due to rigidity offered by the inter and intramolecular crosslinking of gelatin with the epoxy groups of the graft.

Dye Uptake Studies

A spectrophotometric method was used for the quantitative determination of binding of Rosebengal dye to the gelatin-*g*-poly (GMA) system. Percent of dye binding increases with percent of grafting (Table VII); Rosenbengal has a characteristic $n \rightarrow \pi^*$ transition with λ_{max} 546 nm. Figure 1 shows a linear plot of dye uptake versus percent grafting.

Table VII Effect of Percent Grafting [KPS] Variation on Percent Dye Uptake and Percent Swelling

[KPS] × 10 ³ mol/L	Percent Grafting	Percent Dye Uptake	Percent Swelling
1.85	58.8	32.50	309.68
2.59	84.0	52.20	153.33
2.96	103.2	80.50	64.76
3.33	99.3	76.20	75.60

^a [GMA] = 6.8×10^{-1} mol/L; [Gelatin] = 8.3×10^{-4} mol/L; total volume = 100 mL; temperature = 50°C; time = 120 min.

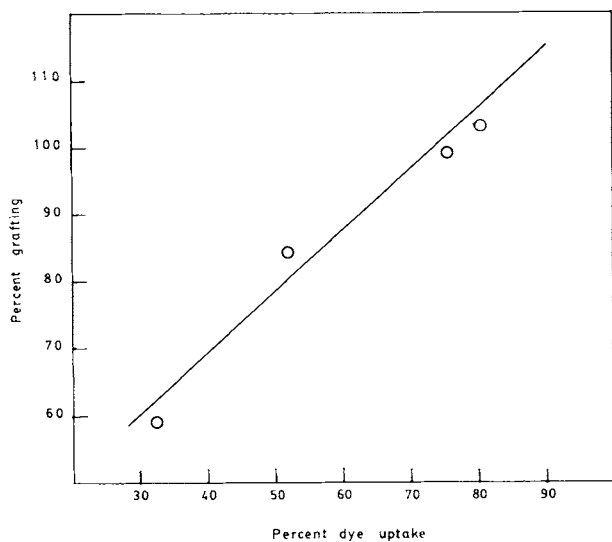


Figure 1 Plot of percent dye uptake vs. percent grafting at different persulfate concentrations.

Swelling Studies

The present investigation produced system of different hydrophilicity based on gelatin-*g*-poly-(GMA). The increased percent grafting decreased the percent swelling because of the increase in hydrophobicity. In the case of peroxy-disulfate concentration (Table VII) percent grafting increased with percent swelling decrease.

FT IR Spectra Analysis

FT IR spectrophotometer has been found to be a valuable tool in studying graft copolymerization reactions. The spectra showed the characteristic of amide absorption at 1650 and 1750 cm^{-1} . The FT IR spectra of grafted and ungrafted polymers are given in Figure 2. The grafted product does not show any characteristic peak corresponding to epoxy group indicating the crosslinking through the epoxy group.

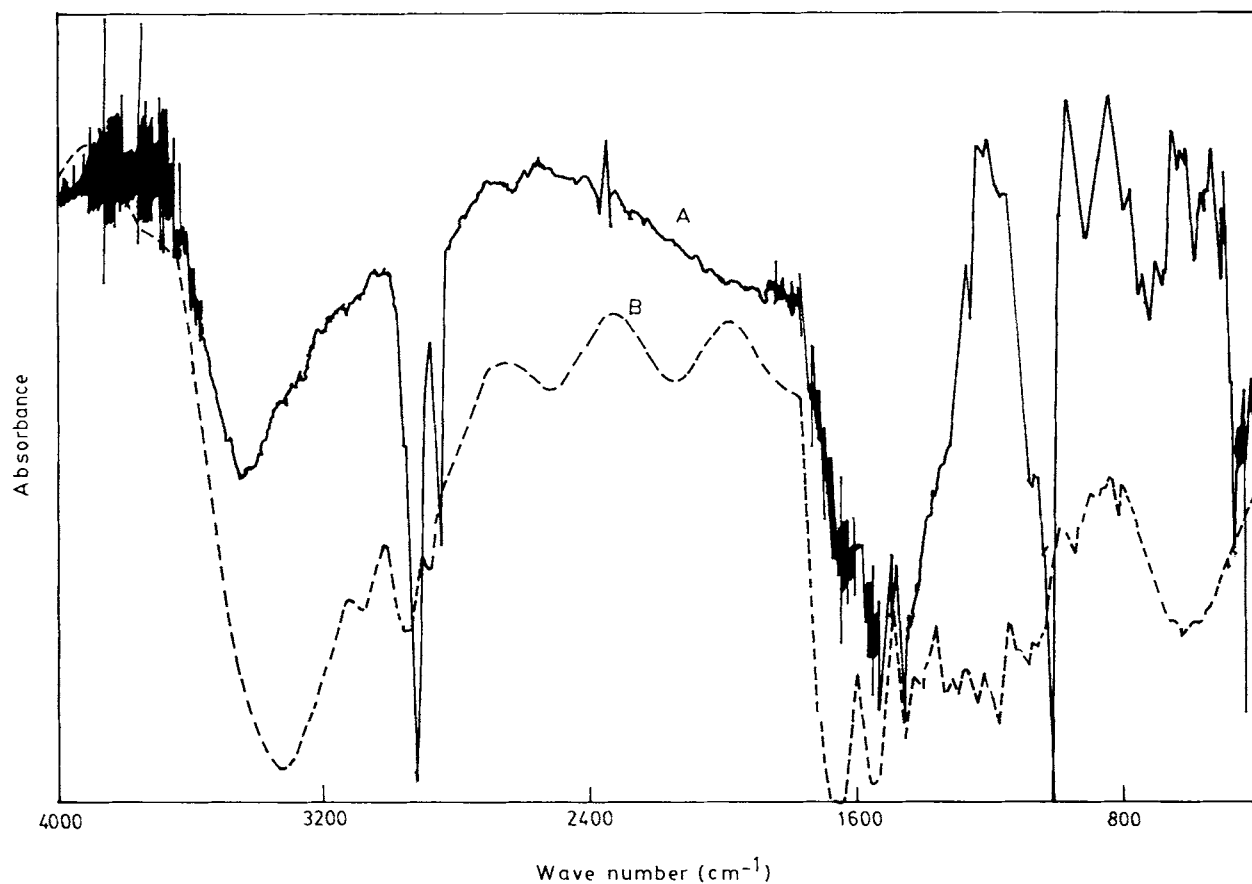


Figure 2 (A) FTIR of pure gelatin. (B) FTIR of gelatin-*g*-poly (GMA).

REFERENCES

1. A. A. Denisova and L. I. Simyakova, *Vysokomol. Soed., Ser. A*, **10**, 357 (1968).
2. Kodak Ltd., Brit. Pat. 841,136 (1960).
3. I. J. Krajswaki, U. S. Pat. 3,291,611 (1966).
4. G. Peieper, O. Bayer, and C. Gloxhuber, Ger. Pat. 1,165,606 (1964).
5. A. Veis, *Macromolecular Chemistry of Gelatin*, Academic Press, New York, 1964.
6. H. Arase and K. Yabuuchi, U. S. Pat. 4,146,398 (1979).
7. M. C. Graffer, U. S. Pat. 4,165,368 (1979).
8. H. Sera, T. Ishil, J. Yamaguchi, and H. Shiraishi, U. S. Pat. 4,173,481 (1979).
9. A. M. Kragh and L. B. Langston, *J. Coll. Sci.*, **17**, 10123 (1962).
10. A. George, G. Radhakrishnan, and K. T. Joseph, *J. Macromol. Sci. Chem.*, **A21**(2), 179 (1984).
11. A. George, G. Radhakrishnan, T. Nagabhushanam, and K. T. Joseph, *J. Macromol. Sci. Chem.*, **A15**(3), 515 (1981).
12. D. Mohan, G. Radhakrishnan, and S. Rajadurai, *Makromol. Chem.*, **183**, 1659 (1982).
13. D. Mohan, G. Radhakrishnan, and S. Rajadurai, *J. Macromol. Sci. Chem.*, **A22**(1), 75 (1985).
14. A. Hebeish, A. Bendak, and A. Kantouch, *J. Appl. Polym. Sci.*, **15**, 2733 (1971).
15. A. Bendak, M. I. Khalil, M. H. El. Rafie, and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 335 (1975).
16. A. K. Pradhan, Advait, G. Panda, N. C. Pati, and P. C. Nazek, *J. Macromol. Sci. Chem.*, **A16**(2), 501 (1981).
17. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.*, **22**, 3003 (1978).
18. G. R. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **23**, 229 (1979).
19. S. Nakamura, E. Yoshikawa, and K. Matsuzaki, *J. Appl. Polym. Sci.*, **25**, 1983 (1980).
20. Meenashi Maruthamuthu and Meenashi Sobhana, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3159 (1979).
21. J. Stejskal, D. Strakova, and P. Kratochvil, *J. Appl. Polym. Sci.*, **36**, 215 (1988).
22. Rakesh Mehrotra and Bengt Ranby, *J. Appl. Polym. Sci.*, **21**, 3407 (1977).
23. Y. Ikada, Y. Nishizaki, I. Sakurada, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1829 (1974).
24. A. George, G. Radhakrishnan, and K. T. Joseph, *J. Polym. Sci. Chem. Ed.*, **23**(11), 2865 (1985).

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