Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Sivakumar, M. , Rajalingam, P. and Radhakrishnan, Ganga(1991) 'Grafting of Hydroxyethyl Methacrylate onto Gelatin', Journal of Macromolecular Science, Part A, 28: 1, 151 — 158
To link to this Article: DOI: 10.1080/00222339108054396
URL: http://dx.doi.org/10.1080/00222339108054396

MACROMOLECULAR REPORTS, A28(SUPPL. 2), 151-158 (1991)

GRAFTING OF HYDROXYETHYL METHACRYLATE ONTO GELATIN

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ABSTRACT

Gelatin was graft copolymerized with poly (hydroxyethyl methacrylate) (HEMA) using potassium peroxydisulphate in aqueous medium. Effect of temperature, 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 backbone concentration. The rate of grafting, grafting efficiency and percent grafting were calculated. The grafting results are discussed in the light of the rate of grafting. Percent Ca^{2+} uptake was carried out on the graft copolymerization and the results are 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. 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[1] combining the desirable properties of both natural and synthetic polymers. The graft copolymerization of butylacrylate onto gelatin has been recently reported[2]. Proteins like gelatin[3,4], casein[5,6], collagen[7], wool[8], silk[9] are modified by grafting various polymers onto them. The modification

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of gelatin by synthetic polymers of biomedical interest should throw more light on the development of new biomaterials[10]. Poly(HEMA) hydrogels are used for biomedical applications[11]. Modified poly(HEMA) have been extensively used in the applications of biocompatibility[12] to calcification[13,14]. The present investigation is based on the grafting of poly(HEMA) onto gelatin with a view to study the calcium binding onto gelatin graft poly(HEMA).

EXPERIMENTAL

Materials

Gelatin(Sigma Chemical Co., USA) and potassium persulphate (Merck,GR) were used as such without further purification. Monomer, Hydroxyethyl methacrylate (Fluka AG) was purified by distillation under vacuum. The middle fraction was used in the experiment.

Procedure

A known amount of gelatin was dissolved in water at constant stirring under nitrogen atmosphere and maintained at the required temperature. After sufficient time hydroxyethyl methacrylate was added followed by the initiator, potassium persulphate. 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.

Ca^{2+} uptake studies

The Ca^{2+} uptake studies of gelatin grafted product were carried out by volumetric analysis.

Calculations

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

1. Percent grafting (PG):

$$\frac{\text{Weight of graft copolymer} - \text{Weight of gelatin}}{\text{Weight of gelatin}} \times 100$$

2. Grafting efficiency (GE)

$$\frac{\text{Weight of graft copolymer}}{\text{Weight of graft copolymer} + \text{Weight of unbound homopolymer}} \times 100$$

3. Rate of grafting (R_g) :

(moles $l^{-1}sec^{-1}$)

$$\frac{\text{Weight of graft copolymer} - \text{Weight of homopolymer}}{\text{Mol.wt. of monomer} \times \text{Time of polymerization in seconds} \times \text{Volume of reaction mixture in ml.}} \times 100$$

4. Percent Ca^{2+} uptake

$$\frac{\text{Uptake of } Ca^{2+} \text{ (mg)}}{\text{Initial weight (mg)}} \times 100$$

RESULTS AND DISCUSSION

The influence of concentration of backbone, monomer, initiator and the effect of temperature on the graft copolymerization of hydroxyethyl 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 6.66×10^{-4} to 11.6×10^{-4} mol.l^{-1} and the results are depicted in Table 1.

Percent grafting and grafting efficiency increased initially with increase in gelatin concentration, reached a maximum value and finally decreased with further increase in gelatin concentration. Similar results are also obtained in the grafting of acrylonitrile onto starch[15] and grafting of acrylonitrile onto gelatin[3]. The initial increase may be due to

TABLE 1

Effect of Gelatin concentration on grafting

[HEMA) = 3.97 x 10^{-1}mol.l^{-1} Total volume = 100 ml

[KPS] = 1.85 x 10^{-3}mol.l^{-1} Temperature = 60°C

Time = 120 min.

[Gelatin] x 10^4 mol.l^{-1}	R_g x 10^6 mol.$l^{-1}$$sec^{-1}$	Grafting efficiency	Percent grafting
6.66	2.22	83.82	94.5
8.33	2.57	84.79	98.2
10.00	3.20	86.80	92.0
11.60	3.13	82.70	90.0

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 2).

Increase in rate of grafting was observed upon increasing the monomer concentration from 3.17 x 10^{-1}mol.l^{-1} to 6.35 x 10^{-1}mol.l^{-1}. Similar results are also obtained in the grafting of ethyl acrylate onto gelatin[16]. It is probably due to gel effect which arises when polymerising medium becomes highly viscous. The 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 grafting and grafting efficiency.

TABLE 2

Effect of HEMA concentration on grafting

[KPS] = 1.85×10^{-3} mol.l^{-1} Total volume = 100 ml

[Gelatin] = 8.33×10^{-4} mol.l^{-1} Temperature = 60°C

Time =120 min.

[HEMA] x10 mol.l^{-1}	$R_g \times 10^6$ mol.l^{-1}sec^{-1}	Grafting efficiency	Percent grafting
3.17	2.33	--	82.60
3.97	2.57	84.71	98.60
4.76	3.16	87.01	134.8
6.35	3.87	86.18	170.4

Effect of initiator concentration

In the present investigation concentration of the initiator was varied from 1.479×10^{-3} mol.l^{-1} to 3.33×10^{-3} mol.l^{-1}. It is seen that percent grafting increased upto critical initiator concentration of 2.77×10^{-3} mol.l^{-1} and then decreased (Table 3) as in the case of potassium persulphate initiated grafting of poly(MMA) onto poly(vinyl alcohol) [17]. This is because of the fact that higher initiator concentration yields greater number of primary radicals, gelatin radicals and growing macroradicals of side chains, which may interact with each other resulting in termination, thus reducing grafting efficiency and percent grafting.

High reactivity is observed that the initiator decomposition is much larger (order with respect to initiator is 1.5) than the case with grafting of acrylonitrile onto gelatin in aqueous zinc chloride medium[2]. In view of the high reactivity of HEMA towards persulphate initiation, considerable amount of homopolymer may be formed and due to the entangled network formation not extractable with acetone by soxhlet extraction.

TABLE 3

Effect of Persulphate concentration on grafting

[HEMA] = $3.97x10^{-1}mol.l^{-1}$ Total volume = 100 ml

[Gelatin] = $8.33x10^{-4}mol.l^{-1}$ Temperature = 60°C

Time = 120 min.

[KPS] = $10^3 mol.l^{-1}$	$R_g \times 10^6$ $mol.l^{-1}sec^{-1}$	Grafting Efficiency	Percent Grafting
1.85	1.65	84.79	98.2
2.22	2.17	85.16	105.4
2.77	4.20	88.32	113.8
3.33	5.17	88.41	107.8

TABLE 4

Effect of Temperature on grafting

[HEMA] = $3.97x10^{-1}mol.l^{-1}$ Total volume = 100 ml

[Gelatin] = $8.33x10^{-4}mol.l^{-1}$ Time = 120 min.

[KPS] = $1.85 \times 10^3 mol.l^{-1}$

Temperature (°C)	Percent grafting
50	81.4
60	98.2
70	94.0
80	83.2

TABLE 5

Effect of Percent Grafting ([Gelatin]) variation) on percent Ca^{2+} uptake

[HEMA] = $3.97 \times 10^{-1} mol.l^{-1}$
[KPS] = $1.85 \times 10^{-3} mol.l^{-1}$
[Ca^{2+}] = $1.54 \times 10^{-2} mol.l^{-1}$

Time = 120 min.
Total volume = 100 ml.
Temperature= 60°C

[Gelatin] $\times 10^{4}$ mol.l^{-1}	Percent Grafting	Percent Ca^{2+} uptake
6.66	94.5	14.61
8.33	98.2	14.94
10.00	92.0	7.80
11.60	90.0	5.20

Effect of temperature

An optimum temperature required for maximum grafting was 60°C. The results are presented in Table 4.

Percent grafting after 60°C, decreased because of coagulation of polymer, decomposition of persulphate and degradation of gelatin at higher temperatures.

Ca^{2+} uptake studies

A volumetric method was used to find out quantitative determination of binding of Ca^{2+} to the gelatin-g-poly(HEMA) system. Percent of Ca^{2+} binding increases with percent of grafting as shown in Table 5.

The binding of Ca^{2+} ions by the graft copolymer have potential applications in the decalcification. Detailed work is in progress for the preparation of grafted microspheres for metal ion removal.

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