

GRAFTING OF 2-HYDROXYETHYLMETHACRYLATE ONTO HIDEPOWDER

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INTRODUCTION

HYDROGELS synthesized from 2-hydroxyethylmethacrylate (HEMA) and other monomers are extensively used as biomaterials for contact lenses, artificial organs, drug carriers etc.¹⁻⁴. However, hydrogels made from pure synthetic materials have less tissue tolerance and blood compatibilities. The tissue tolerance can be increased if the synthetic materials are coupled with natural biomaterials.

Graft copolymerization of HEMA onto soluble collagen in the presence of ceric ion is a viable system which can produce a compatible hydrogel material. In this laboratory, work is under progress to synthesize hydrogels, by grafting of HEMA and copolymers of HEMA with other vinyl monomers, onto soluble collagen. In this report, preliminary studies of graft copolymerization of HEMA onto insoluble collagen in the presence of ceric ion are given.

EXPERIMENTAL

Materials

Hydroxyethylmethacrylate (FLUKA) was purified with 10% sodium hydroxide, washed with distilled water until free from alkali, dried over anhydrous magnesium sulphate and then distilled under vacuum. The middle fraction of the distillate was used for the grafting reaction. Ceric ammonium nitrate (Baker, USA.) was dissolved in 1N nitric acid so as to give appropriate concentration of ceric ion. Collagen prepared from the middle corium of buffalo hide was used as the source of insoluble collagen.

Grafting Procedure

Grafting reactions were carried out in double walled glass reaction tubes and charged with a weighed amount of hidepowder dispersed in 25 ml of distilled water. The contents were stirred continuously with a magnetic stirrer and the temperature of the reaction was maintained at 28° C by circulating water from a thermostatic water bath. After proper dispersion, the required quantity of the monomer was added and oxygen free nitrogen was bubbled for about 15 min. Calculated quantity of the initiator was then added to the system making the volume 37 ml and nitrogen flow was stopped, allowing the reaction in nitrogen atmosphere for about 3 hr, after which the contents were poured into ice-cold water, filtered through a weighed sintered glass crucible and dried in vacuum.

Isolation of graft copolymer

With a view to evaluating the percent grafting and grafting efficiency, tumbled bottle method was adopted for the separation of the graft copolymer from the ungrafted copolymer using methanol as the solvent. It was difficult to separate out ungrafted backbone, since the backbone used in this experiment was the insoluble collagen. Hence, it is assumed that the entire backbone is involved in the grafting reaction. After the separation of the ungrafted homopolymer, the samples were dried to constant weight. The extraction of ungrafted poly HEMA and the weight increase over that of backbone is an indication of the establishment of grafting reaction. The percent grafting and grafting efficiency were calculated as follows:

TABLE I

Graft copolymerization of HEMA onto insoluble collagen using ceric ammonium nitrate as initiator

Sl. No.	Weight Ratio of backbone: Monomer	Per cent grafting	Grafting efficiency	$R_p \times 10^6$ moles $l^{-1} s^{-1}$	$R_g \times 10^6$ moles $l^{-1} s^{-1}$	$R_h \times 10^6$ moles $l^{-1} s^{-1}$	R_g/R_h = G.E. × 100	R_g/R_h
1.	1:1	1.10	8.3	1.28	0.11	1.18	8.3	0.09
2.	1:2	9.11	31.6	2.80	0.88	1.91	31.6	0.46
3.	1:3	19.92	43.0	4.57	1.93	2.64	42.2	0.73
4.	1:4	32.86	31.1	10.20	3.17	3.17	31.1	0.45

Effect of monomer concentration

HIDE POWDER = 0.5 g
[CAN] = 6.77×10^{-3} mole/litre

Time = 3 hr
Temperature = 28° C
Total Volume = 37 ml

$$\text{Percent grafting} = \frac{\text{Weight of the grafted poly HEMA}}{\text{Weight of hide powder}} \times 100$$

$$\text{Grafting efficiency} = \frac{\text{Weight of the grafted poly HEMA}}{\text{Weight of grafted poly HEMA} + \text{weight of ungrafted poly HEMA}} \times 100$$

From the values of the total poly HEMA, the weight of grafted side chain and ungrafted poly HEMA, R_p , R_g and R_h were calculated where R_p , R_g and R_h indicate the rates of polymerization, grafting and homopolymerization respectively.

RESULTS AND DISCUSSION

The values of the percent grafting and grafting efficiency as a function of monomer concentration at a given concentration of initiator and backbone are given in table 1. According to Smets *et al*⁵ grafting efficiency may also be described by the ratio of R_g/R_h and the corresponding values are also included in table 1. From these results (table 1) the percent grafting of HEMA onto collagen was found to increase steadily as the monomer concentration was enhanced. However, the grafting efficiency was found to increase upto 1:3, weight ratio of backbone to monomer and with a further increase in monomer concentration the grafting efficiency was found to decrease. The increase in the percent grafting, with the monomer concentration may be attributed to the increase in the rate of grafted side chains. The decrease in grafting in grafting efficiency may be due to this rate of formation of polyHEMA being higher than that of grafting of polyHEMA onto the backbone.

It has been established that ceric ion reversibly complexes with secondary hydroxyl groups⁶ and in the dissociation of this complex, ceric ion is reduced to cerous and the hydrogen atom is oxidized. During this process, a free radical active centre is formed on the backbone chain which induces the graft copolymerization in natural polymers like starch, cellulose, wool,

collagen etc. It is believed that ceric ion initiation is highly specific to hydroxyl group containing materials.

HEMA contains a primary hydroxyl group and to ensure the formation of homopolymers of HEMA in the absence of backbone, an experiment was carried out and sufficient homopolymer formation was noticed. This indicates that ceric ion initiates the homopolymerization of HEMA—the active centre being the hydroxyl group of HEMA. This free radical chain transfer reaction is responsible for the decrease in the grafting efficiency as the monomer concentration is increased, at constant backbone and initiator concentrations. The results are similar to those of Fanta⁶ in the graft copolymerization of acrylonitrile onto unswollen starch using ceric ammonium nitrate as the initiator. When unswollen wheat starch was allowed to react with ceric ammonium nitrate in a minimal amount of water first and then in a solution of acrylonitrile in methanol and assuming that methanol entered into free radical chain transfer reaction, it was found that the conversion of the monomer into ungrafted polyacrylonitrile was relatively high.

ACKNOWLEDGEMENTS

Financial assistance by CSIR, New Delhi in the form of a fellowship to one of the authors (SA) is gratefully acknowledged. The authors are grateful to Dr. N. Ramanathan, Director, CLRI, for his keen interest in this work.

1. Refojo, M. F., *J. Biomed. Mater. Res.*, 1971, 5, 113.
2. Bruck, S. D., *J. Biomed. Devices, Artif. Organs*, 1978, 6, 57.
3. Tollar, M., Stol, M. and Kliment, K., *J. Biomed. Mater. Res.*, 1969, 3, 305.
4. Hofmann, A. S., *Radiation Phys. Chem.*, 1977, 9, 207.
5. Smets, G. Claesan, J., *J. Polym. Sc.*, 1952, 8, 209.
6. Fanta., G. F. In *Block and graft copolymerization* (ed.) R. J. Ceresa, Vol. 1, John Wiley, London, New York, Sydney, Toronto, 1973, p 3 and 7.