Photosensitized Grafting of Acrylamide and Hydroxyethyl Methacrylate onto Cellulose

M. ALVES DA SILVA, M. HELENA GIL, and ELISA LAPA, *Departamento de Quimica da Universidade de Coimbra, 3049 Coimbra, Portugal* and J. T. GUTHRIE, *Department of Colour Chemistry, Leeds University, Leeds, LS2 9JT England*

Synopsis

The photoinitiated copolymerization of acrylamide and hydroxyethyl methacrylate onto cellulose substrates, from acetone/water solutions, was studied using isopropyl thioxanthone as the photoinitiator. The graft copolymerization was carried out over a range of monomer and photoinitiator concentrations. Grafting is shown to be dependent on the nature of the monomer and the concentration of monomer and photoinitiator. In the case of acrylamide, it was found that there is an optimum concentration of the photoinitiator for grafting to occur effectively. The kinetics of graft copolymerization were studied in some detail and the results are considered.

INTRODUCTION

The photosensitized grafting of vinyl and acrylic monomers onto a range of polymeric substrates has been the subject of particular interest in the recent past. Much of this interest originates in the recognition that many of the copolymeric products possess an interesting range of physical and/or chemical properties.[1] The general features of photopolymerization reactions associated with grafting have been reviewed elsewhere, though only with reference to largely nonaqueous systems.[2]

With the development of water-soluble, efficient, photosensitizers of polymerization reactions, attention has been given to grafting reactions, in largely aqueous media, involving hydrophilic substrates. Thus, Bottom et al.[3,4] have examined the photosensitized grafting of hydroxyethyl methacrylate onto regenerated cellulose film using a series of novel, water-soluble photoactivators based on the benzophenone and on the benzil chromophore.[3] Their work was extended to include the influence of H-donors on the photodecomposition of these water-soluble photoactivators. This extension arose from the suspicion that grafting arose as a consequence of H-abstraction from the cellulose substrate. The mechanism for such behavior was clearly outlined.

Related studies have been carried out on woollen substrates,[5] cellulose derivatives,[6] pectin,[7] and synthetic supports.[8] Obviously many more variations are possible. Those quoted provide a reasonable background to a technology which is rapidly increasing in importance.

Our interest in copolymeric species lies in their value as supports for immobilization especially in terms of biomedical and bioassay applications. Other areas include affinity chromatographic separations, food processing, and so on.[9,10] Hitherto the approaches we have adopted, for making supports for

Journal of Applied Polymer Science, Vol. 34, 871–880 (1987)

CCC 0021-8995/87/020871-10$04.00

immobilization, have largely concerned production via high energy, radiation-induced grafting reactions onto hydrophilic[11] and also onto hydrophobic[12] substrates.

Here we report our work on the photosensitized grafting of acrylamide and of hydroxyethyl methacrylate onto cellulose substrates using aqueous media, under heterogeneous conditions with respect to the substrate. The developed systems have potential in a variety of immobilization studies.

EXPERIMENTAL

Reagents

Regenerated cellulose film was supplied by Cifa, Oporto, Portugal. This was boiled in deionized water for one hour, with several water changes, to remove plasticizers and any other additives. The extracted cellulose was washed with methanol and dried to constant weight at 313 K under vacuum. Extreme care was taken to ensure that the prepared films were maintained in a crease-free condition throughout.

Acrylamide (AM) and 2-hydroxyethyl methacrylate (HEMA) were obtained from BDH Ltd., Poole, Dorset, UK. These were used as supplied, i.e., no attempt was made to remove the inhibitor. Previous experimentation has shown that this inhibitor prevents homopolymerization but does not influence the grafting reaction. Thus, the presence of the inhibitor gives reduced problems in copolymer purification. The photoinitiator, isopropyl thioxanthone (ITX) was supplied by Ward-Blenkinsop and Co. Ltd. (Halebank, Widnes, Cheshire, UK) and was used as supplied.

GRAFTING PROCEDURES

The purified cellulose films have a density of 1.4 kg dm^{-3} which gave ease of handling in the impregnation medium. This medium, acetone/water (50 : 50) was used as the solvent for each of the monomers and also for the photoactivator, (ITX). Efficient solution of the initiator involved dissolving it initially in a known quantity of acetone and then adding deionized water. Solutions of initiator, prepared in this way, were both physically and chemically stable until photoexcited.

The purified cellulose film samples (0.1 g) were separately impregnated with solutions containing monomer and photoinitiator in the concentrations required for the specific study being undertaken. The volume of monomer/photoactivator solution was maintained at 50 cm^3 in each instance. Irradiation was provided by a water-cooled, medium pressure lamp assembly which provided an output of 200 W per inch.

After various known times of irradiation in the presence of air, each series of irradiated film was thoroughly washed with acetone/water (50 : 50) and then treated to an extraction procedure to remove any trace quantities of unwanted, attendant hompolymer and residual monomer. In the extraction procedure, water was used to remove acrylamide and poly(acrylamide) and methanol was used to remove HEMA and poly(HEMA). The copolymer samples were dried to constant weight at 313 K under vacuum. Each system was studied in triplicate.

The range of monomer concentrations and photoinitiator concentrations examined in this study can be summarized as follows.

	Monomer dependence of grafting	
System:	Isopropyl thioxanthone	acrylamide
[M]	—	0.35 to 1.40 mol dm^{-3}
[I]	1.9×10^{-3} mol dm^{-3}	—
	Initiator dependence of grafting	
System:	Isopropyl thioxanthone	acrylamide
[I]	0.4 to 1.9($\times 10^{-3}$) mol dm^{-1}	—
[M]	—	0.35 mol dm^{-3}
	Monomer dependence of grafting	
System:	Isopropyl thioxanthone	2-hydroxyethyl methacrylate
[M]	—	0.12 to 0.77 mol dm^{-3}
[I]	1.9×10^{-3} mol dm^{-3}	—
	Initiator dependence of grafting	
System:	Isopropyl thioxanthone	2-hydroxyethyl methacrylate
[I]	0.9 to 3.9($\times 10^{-3}$) mol dm^{-3}	—
[M]	—	0.19 mol dm^{-3}

RESULTS AND DISCUSSION

Monomer Dependence

The influence of the monomer concentration was studied for an initiator concentration of 1.9×10^{-3} mol dm^{-3}. The variation in the level of grafting

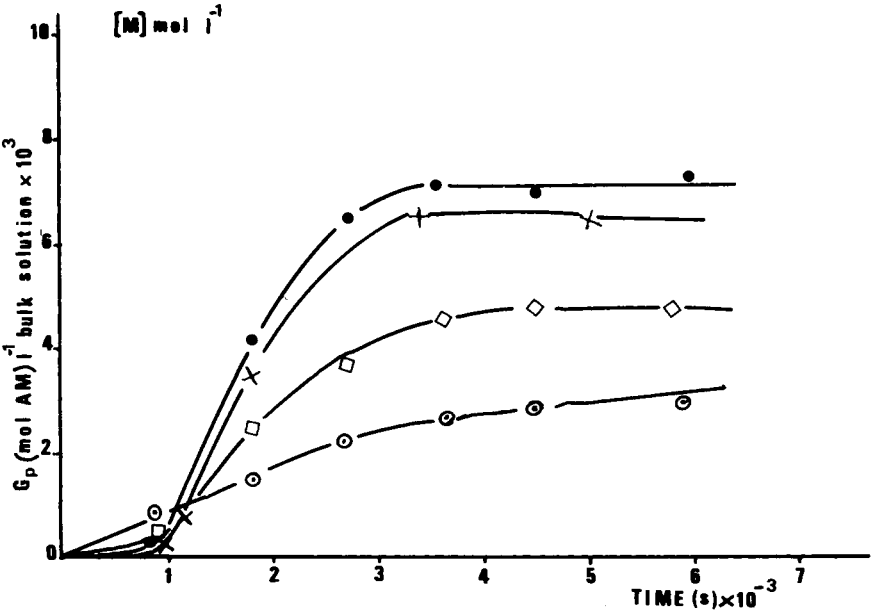

Fig. 1. Variation in the extent of grafting (G) of acrylamide onto cellulose film with time of irradiation for different monomer concentrations: (•) 1.40; (×) 1.05; (□) 0.70; (⊙) 0.35.

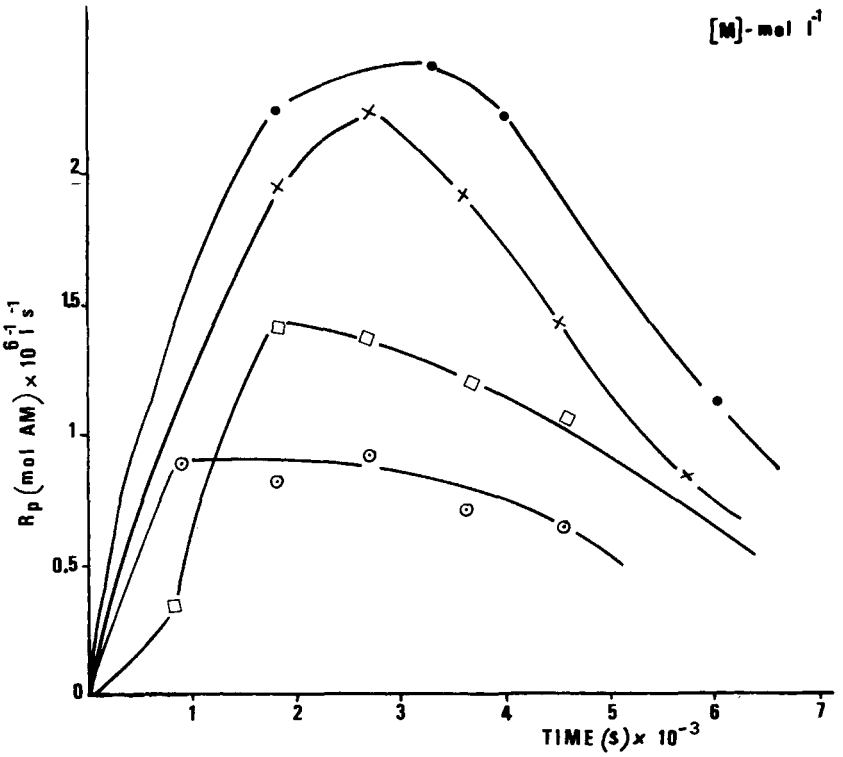

Fig. 2. Variation in the rate of grafting (R_G) of acrylamide onto cellulose film with time of irradiation for different monomer concentrations: (•) 1.40; (×) 1.05; (□) 0.70; (⊙) 0.35.

of acrylamide (AM) onto the cellulose film with time, for the different bulk monomer concentrations, is shown in Figure 1. This shows that when acrylamide is grafted onto cellulose film, the grafting yield increases with increase in the bulk concentration and with time, but after 3500 seconds the yield of grafting levels out in each instance. The variations in the rates of graft copolymerization with time and with the bulk of monomer concentration are shown in Figure 2. Initially the rate of grafting increases and, after a certain time (dependent on the monomer concentrations), decreases.

Figure 3 gives the variation in the level of grafting of HEMA onto cellulose with time and with change in the concentration of HEMA for a bulk initiator concentration of 1.9×10^{-3} mol dm^{-3}. The variation in the rates of grafting with time for different bulk monomer concentrations (HEMA), is shown in Figure 4. For lower HEMA concentrations, the rate of grafting shows an initial decrease with time. However, for higher HEMA concentrations the rate of grafting increases with time, after $\simeq$ 2000 seconds.

It is reasonably clear that both systems give rise to data which cannot be manipulated in such a way as to provide meaningful initial rates of grafting. However the relationships expressed in Figures 1 to 4 have significance in various ways.

We may recall that the grafting levels are expressed as moles of monomer grafted per unit volume of bulk medium. The cellulose is assumed to be an integral part of the total system. The volume of cellulose present in each

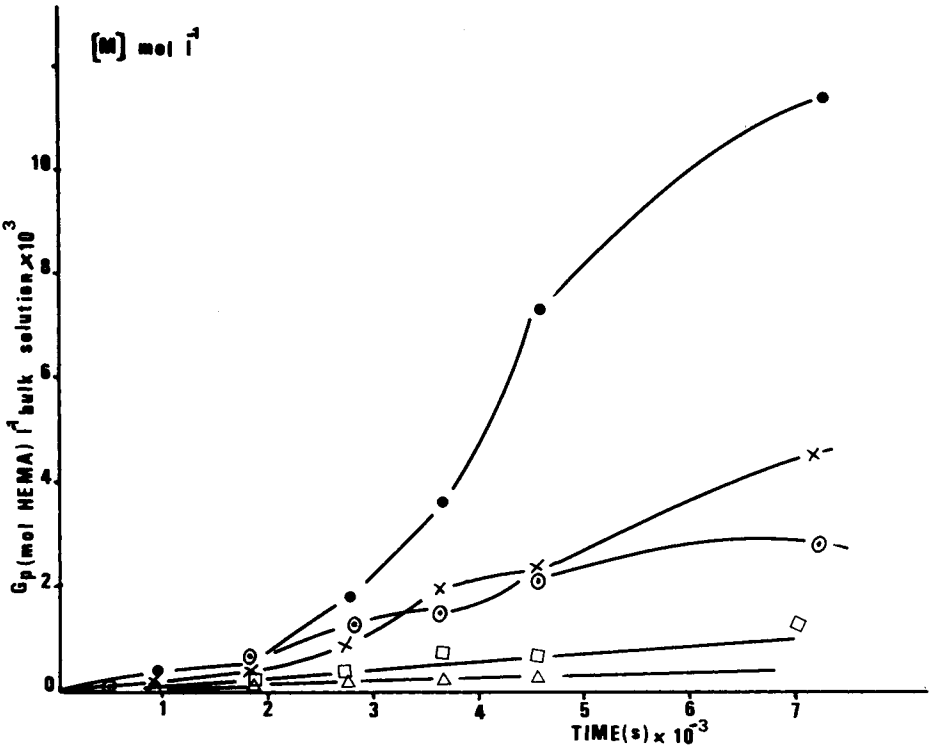

Fig. 3. Variation in the extent of hydroxyethyl methacrylate grafting onto cellulose film with time of irradiation for different monomer concentrations: (•) 0.77; (×) 0.58; (⊙) 0.38; (□) 0.19; (△) 0.12.

system can be obtained from the mass and the density.[1,3] Additivity of volumes is assumed to be a reasonable proposal in each instance. While such manipulations may be convenient in providing a method of expressing quantitative changes, they clearly cannot be used to justify physical situations. The results obtained indicate the heterogeneous nature of the grafting system and suggest that grafting is a surface area-dependent phenomenon.

Figures 5 and 6 relate to the initiator dependence of the extent of grafting of acrylamide onto the regenerated cellulose films. A similar approach was adopted in the generation of the data displayed in Figures 7 and 8, which relate to the initiator dependence of grafting hydroxyethyl methacrylate onto the cellulose film. Figures 5 and 7, indicating changes in the extent of grafting with time and change in initiator concentration, show reasonably linear relationships throughout the initiator concentration range. Anticipated effects are seen in that there is a logical progression in increase in extent of grafting with increase in the initiator concentration. The tendency toward leveling-off effects with increasing time is far less pronounced than was observed with the monomer dependence study. Nonetheless, there is pronounced curvature in the relationships especially at extended times.

Before considering any interpretations of the data presented in Figures 2, 4, 6, and 8, which denote changes in the rate of grafting of the two monomers under various conditions, we must consider the nature of the systems under study.

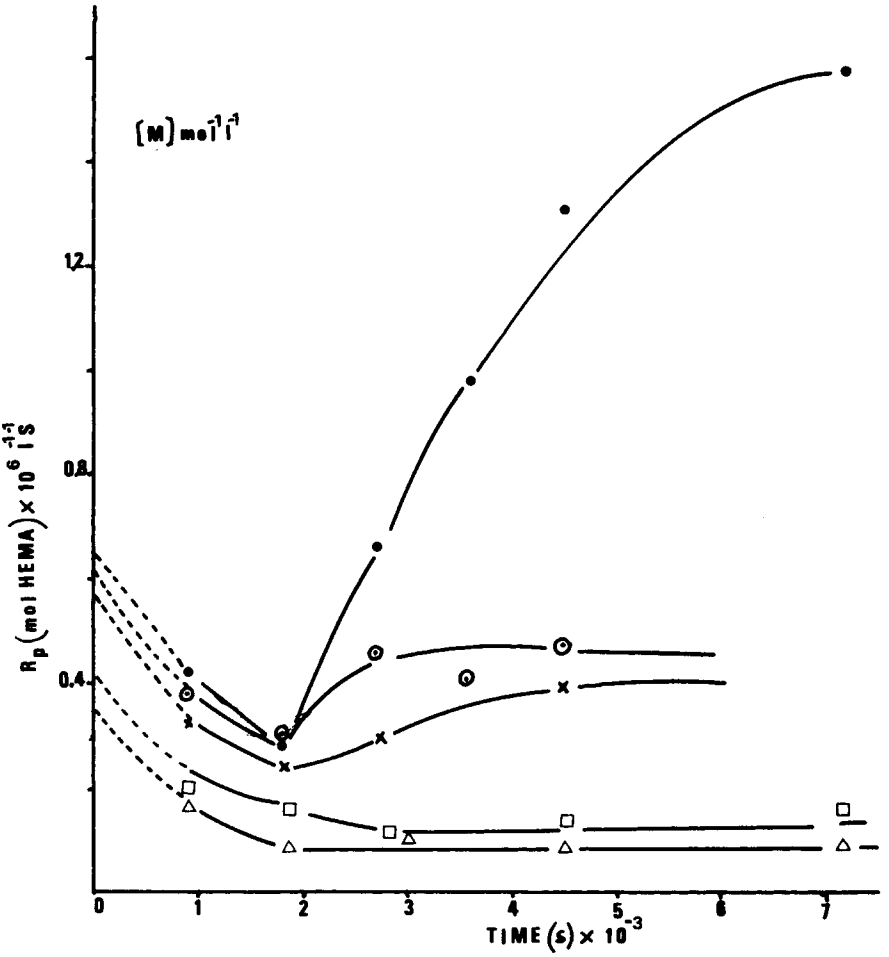

Fig. 4. Variation in the rate of grafting (R_G) of hydroxyethyl methacrylate onto cellulose film with time of irradiation for different monomer concentrations: (•) 0.77; (⊙) 0.58; (×) 0.38; (□) 0.19; (△) 0.11.

Isopropyl thioxanthone is an initiator which requires a synergist for efficient operation.[5] It is also effectively water insoluble, having relatively little affinity for hydrophilic supports. Solubility for the monomer and initiator is provided by the mixed solvent system, though there is evidence to suggest that both AM and HEMA have greater affinity for water than for acetone.[3] Regenerated cellulose film is present in this system as the heterogeneous support, providing a surface for grafting. Radicals are generated at the surface via hydrogen abstraction reactions. Such abstraction involves complex formation between the initiator and the cellulose.

Monomer addition to the reactive sites is the basis of the propagation reaction. However, growing chains will have a high affinity for the cellulose. This could cause a marginal coating action to take place thus blocking the surface from access by initiator and monomer. Under such circumstances the grafting reaction would be expected to maximize in the rate at which it occurs, with respect to time. This implies that at some intermediate stage, there is a

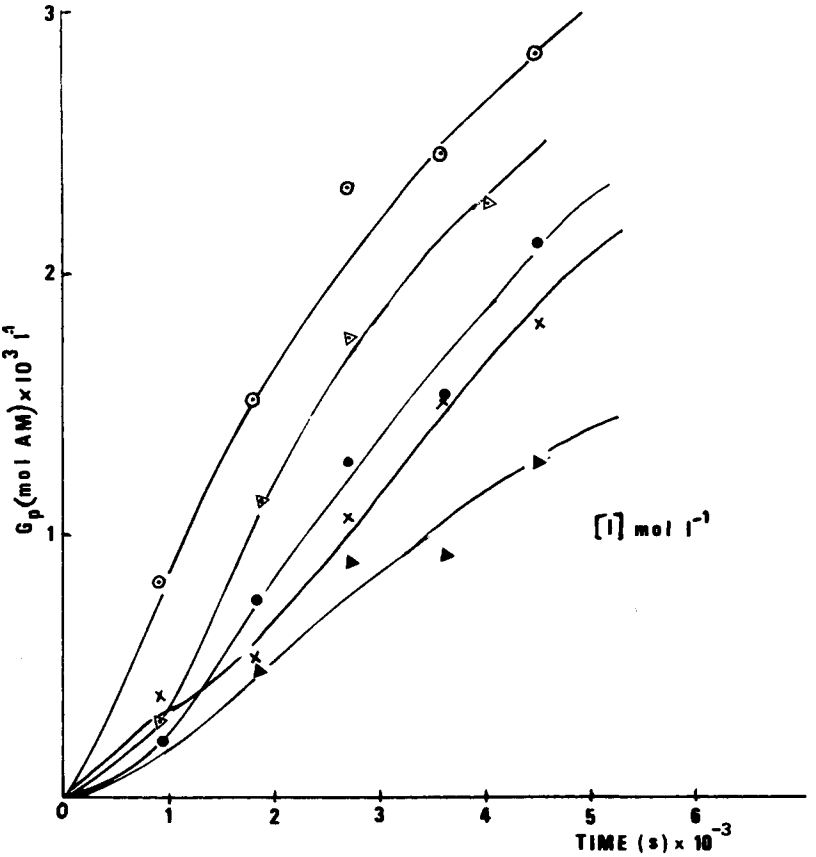

Fig. 5. Variation in the extent of grafting (G) of acrylamide onto cellulose film with time of irradiation for different initiator concentrations: (⊙) 1.9×10^{-3}; (▲) 2.9×10^{-3}; (●) 3.9×10^{-3}; (×) 0.9×10^{-3}; (▲) 0.4×10^{-3}.

reduction in the dependency of grafting on the particular experimental variables.

Figure 2 shows a clear maximum in the rate of grafting with time throughout the monomer concentration range involving acrylamide. However, a pronounced minimum is seen in Figure 4 when hydroxyethyl methacrylate is being grafted. This difference in behavior may be explained by considering the physical character of the two monomers. Acrylamide is highly water soluble owing to the presence of the amide group. Compared with acrylamide, hydroxyethyl methacrylate could be considered to have a significant degree of hydrophobicity leading toward surface-active character. Such activity could bring a degree of orientation of the monomer in its approach to the reactive site. One might surmise that acrylamide is grafting in a manner which is indicative of Langmuir-type phenomena. With hydroxyethyl methacrylate, satisfactory approach of the monomer to the surface of cellulose may require a critical concentration of monomer, otherwise the low monomer concentration will favor a high level of interaction between hydroxyethyl methacrylate and water.

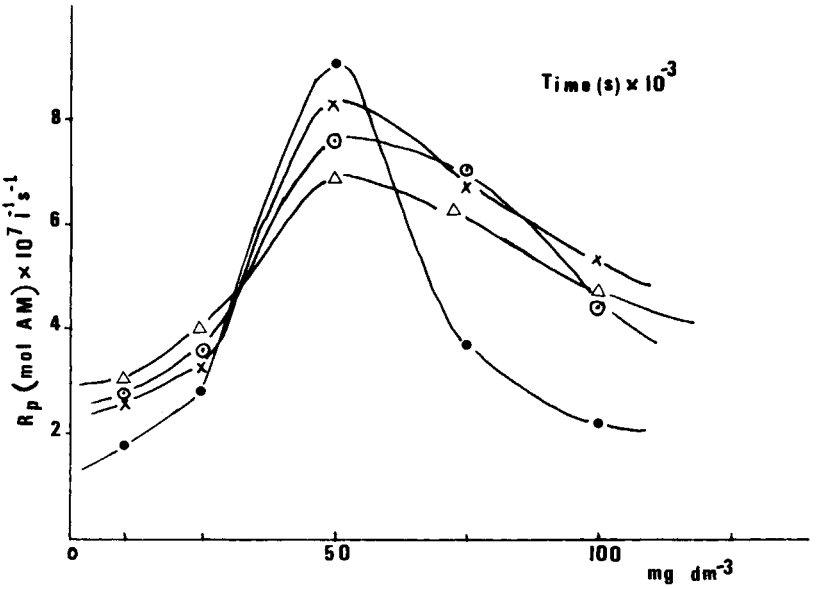

Fig. 6. Variation of the rate of grafting of acrylamide onto cellulose film with initiator concentration (mg/dm^3) for different times of irradiation: (•) 0.9; (×) 1.8; (⊙) 2.7; (△) 3.6.

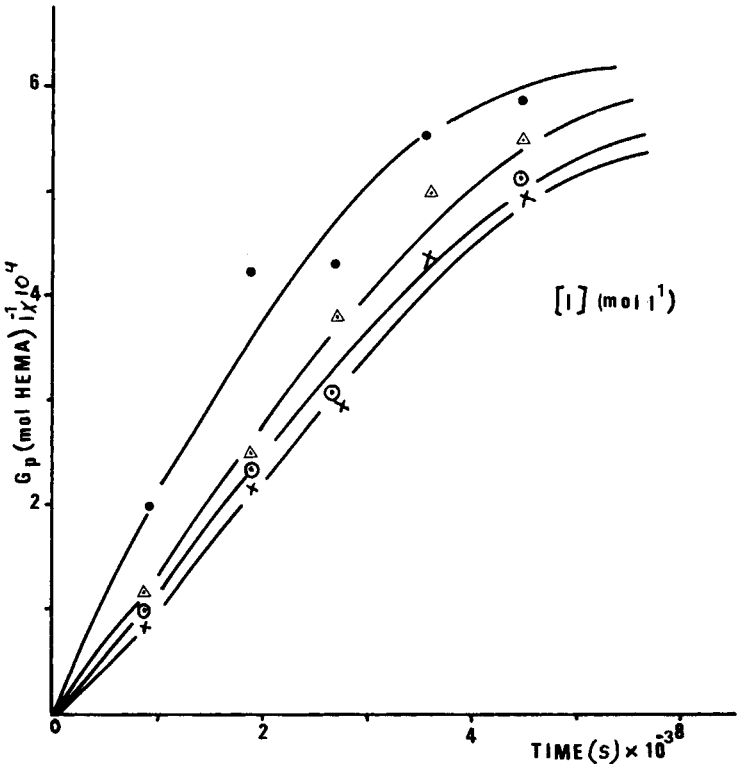

Fig. 7. Variation in the extent of grafting (G) of hydroxyethyl methacrylate onto cellulose film with time of irradiation for different initiator concentrations: (•) 3.9×10^{-3}; (△) 2.9×10^{-3}; (⊙) 1.9×10^{-3}; (×) 0.9×10^{-3}.

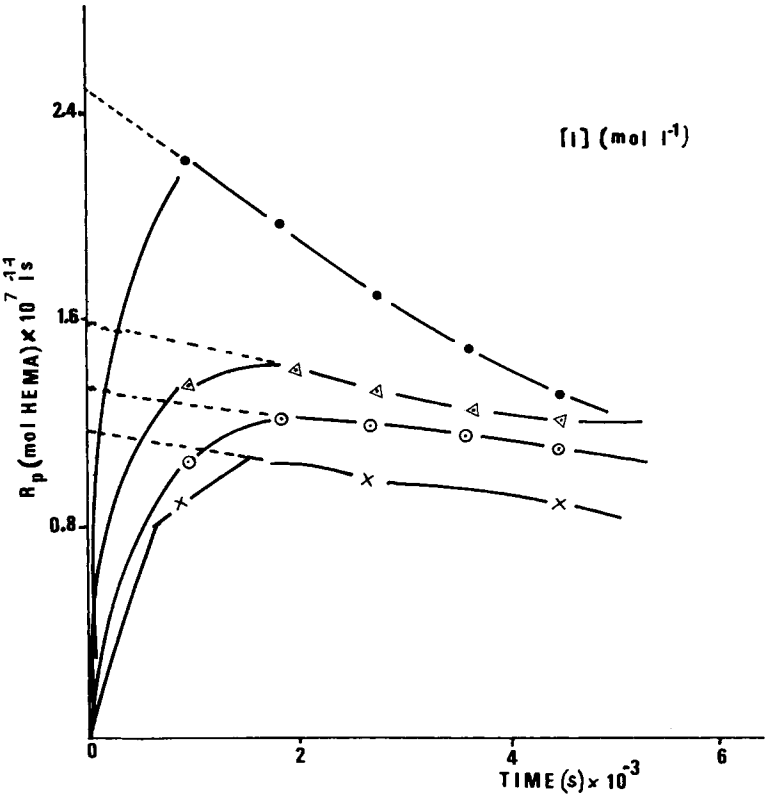

Fig. 8. Variation in the rate of grafting (R_G) of hydroxyethyl methacrylate onto cellulose film with time of irradiation for different initiator concentrations: (●) 3.9×10^{-3}; (△) 2.9×10^{-3}; (⊙) 1.9×10^{-3}; (×) 0.9×10^{-3}.

Such factors are of importance when one bears in mind the potential application of these kinds of copolymeric material.

Thus, the various types of biocatalyst immobilization procedure owe their success or otherwise to the nature of the support system both from the physical and the chemical point of view. Photoinitiated grafting of selected monomers can provide useful binding sites on the surface of substrates. Control over the surface hydrophilicity/hydrophobicity can be achieved. However it is important that attention be paid to kinetic/mechanistic factors throughout substrate preparation.

We gratefully acknowledge the financial assistance provided by Junta Nacional de Investigacao Cientifica e Tecnologica, Lisboa, in support of this work.

References

1. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, Heidelberg, 1981.
2. M. K. Mishra, *J. Macromol. Sci. Rev. Macromol. Chem. C.*, **19** (2), 193 (1980).
3. R. A. Bottom, P. Green, and J. T. Guthrie, *Polym. Photochem.*, **6**, 111 (1985).
4. R. A. Bottom, P. Green, and J. T. Guthrie, *Polym. Photochem.*, **6**, 59 (1985).

5. P. Barker, M. J. Davis, A. A. Godfrey, P. Green, and J. T. Guthrie, *J. Appl. Polym. Sci.*, **26**, 521 (1981).
6. F. I. Abdel-Hay, J. T. Guthrie, and M. Ryder, *Polym. Bull.*, **1**, 501, (1979).
7. C. G. Beddows, M. H. Gil, and J. T. Guthrie, *Polym. Bull.*, **11**, 1 (1984).
8. S. Tazuke and H. Kimura, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 497 (1978).
9. F. I. Abdel-Hay, C. G. Beddows, M. H. Gil, and J. T. Guthrie, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2463 (1983).
10. C. G. Beddows, M. H. Gil, and J. T. Guthrie, *Polym. Bull.*, **14**, 199 (1985).
11. C. G. Beddows, M. H. Gil, and J. T. Guthrie, *Polym. Photochem.*, **7**, 213 (1986).
12. C. G. Beddows, M. H. Gil, and J. T. Guthrie, *Polym. Photochem.*, **7**, 83 (1986).

Received August 5, 1986
Accepted December 17, 1986