

## PHOTOSYNTHETIC MEMBRANES II: KINETIC STUDIES OF PHOTOINITIATED GRAFTING OF SOME ACRYLIC MONOMERS ONTO CELLULOSE

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### Summary

Photochemical grafting of 1,6-hexanediol diacrylate, diethylene glycol diacrylate and tetraethylene glycol diacrylate onto cellulose in the form of filter paper was investigated kinetically at  $30 \pm 2$  °C with 1,2-diphenyl-2,2-dimethoxyethanone as a photoinitiator, under experimental conditions suitable for the preparation of membrane systems. Irradiations were carried out polychromatically, with incident radiation of flux  $(2.5 \times 10^{-8}) - (22.6 \times 10^{-8})$  einsteins  $s^{-1} cm^{-2}$ . The ratio  $R$  between the molar concentrations of photoinitiator and monomer were varied between 0.005 and 0.095, while the  $n/S$  value ( $n$ , moles of diacrylate monomer deposited per unit apparent surface  $S$ ) was varied between 7.61 and  $75.0 \mu mol cm^{-2}$ . Two consecutive constant-rate processes were indicated by the kinetic curves. The quantum yields  $\Phi_1$  and  $\Phi_2$  for the first and second constant-rate periods were calculated. They are almost insensitive to the difference in diacrylate monomer structure; the  $\Phi_1$  show a linear dependence on  $R$ , while the  $\Phi_2$  show an inverse dependence on  $n/S$ . The relevance of photochemical parameters in the proposed reaction mechanism is discussed.

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### 1. Introduction

There has been considerable interest during recent years in the possibility of improving cellulose and cellulosic materials by grafting [1] with a suitable monomer either by chemical means or via high energy, UV or visible radiation.

UV-radiation-induced processing of cellulose is now well established in several fields [2], including the curing of surface coatings and the drying of printing inks. Recently, it has also been applied to impart functional proper-

ties to textiles and to obtain wrinkle-resistant and flame-retardant cotton fabrics [2], as well as to enhance water sorbency [3] or to help conserve aged paper [4].

Since the first studies in the field, which were performed in the early 1960s using anthraquinone [5, 6] as the sensitizer, a considerable amount of work has been done. Ogiwara and Kubota have extensively investigated the effect of wavelength [7, 8], solvent [9],  $H_2O_2$  [10] or metal ions [11] on the photoinduced graft copolymerization of methyl methacrylate onto cellulose. Extensive research has also been carried out by Guthrie *et al.* on a styrene-cellulose graft copolymer obtained by the mutual irradiation technique [12, 13], as well as on other cellulosic copolymers obtained by UV irradiation [14 - 16].

In recent years our research group has been involved in kinetic studies on photoinduced grafting of acryloxy-substituted azo dyes onto synthetic polymers [17 - 23] as well as onto cellulose [24]. Technologically acceptable rates of photochemical reaction have been reached in the presence of diacrylate comonomers and a photoinitiator [22]. Some specimens obtained under these conditions and grafted onto polypropylene ribbon were demonstrated to behave as membrane systems for gas separation (see ref. 23, which may be considered as Part I of this series).

In the present work, the kinetics of photoinduced grafting onto cellulose of three diacrylate monomers has been investigated systematically in order to obtain further mechanistic information on this process under experimental conditions which are suitable for the preparation of membrane systems.

## 2. Experimental details

Cellulose, in the form of filter paper ("black band", Schleicher and Schüll, F.R.G.) was employed as a model for a macroporous substrate.

1,6-Hexanediol diacrylate (I) (UCB, Belgium), diethylene glycol diacrylate (II) and tetraethylene glycol diacrylate (III) (Sartomer, U.S.A.), as well as 1,2-diphenyl-2,2-dimethoxyethanone (IV) (Fratelli Lamberti, Italy) were commercial products. They were used as received, without further treatment or purification.

Reagent grade acetone was purified by addition of sodium hydroxide and potassium permanganate, and was successively dried by refluxing and distilling over sodium under a stream of nitrogen.

1 ml of a solution (solvent, dry acetone) of one of the diacrylate monomers I, II or III (0.215 - 2.15 M) plus the photoinitiator IV ( $R = [IV]/[\text{monomer}]$  varied in the range 0.005 - 0.095) was uniformly deposited by standard procedures using a microsyringe dispenser on a cellulose disk of diameter 6 cm, and the solvent was evaporated at room temperature in a desiccator under vacuum (0.1 mbar). Irradiations were effected with a 2000 W high pressure mercury arc lamp (Hanovia, F.R.G.) which was fitted with a

reflector of semielliptical cross-section and placed in a suitable housing, in which the distance from the irradiated samples could be regulated for the incident radiation flux to range from  $(2.5 \pm 0.2) \times 10^{-8}$  to  $(22.6 \pm 0.8) \times 10^{-8}$  einsteins  $s^{-1} cm^{-2}$ . The system was placed inside a cooled glove box and oxygen was excluded by passing through a stream of purified nitrogen (oxygen content, below 0.3 ppm). The temperature of the reacting system increased to about  $30 \pm 1.5$  °C during irradiation. After the desired irradiation time, the sample was Soxhlet extracted with acetone, which removed efficiently non-reacted monomers and ungrafted homopolymers.

Graft yields as a function of time were obtained as the ratio between the amount of monomer grafted and that initially deposited onto the surface. The amount of grafted monomer was calculated by subtracting the amount of non-reacted monomer and ungrafted homopolymer, determined by gravimetric analysis of the Soxhlet-extracted acetone solution, from the amount of monomer initially deposited onto the surface. An appropriate aliquot of this solution was completely evaporated on a small aluminium disk by an IR lamp. The whole solute content was corrected for the residual presence of photoinitiator, determined by spectrophotometry analysis (a Varian DMS-90 Plus spectrophotometer was employed). The presence of photoproducts deriving from IV was found to interfere by no more than 1% - 2% in the final result of the gravimetric analysis carried out by this means.

Irradiation fluxes and quantum yields were measured by potassium ferrioxalate actinometry, according to the method of Hatchard and Parker [25]. Quantum yields were corrected for unabsorbed energy in each case.

### 3. Results and discussion

Photochemical grafting of I, II and III onto cellulose, in the presence of IV as a photoinitiator, were investigated kinetically at  $30 \pm 2$  °C. Irradiation was carried out polychromatically with incident radiation of flux  $(2.5 \pm 0.2) \times 10^{-8}$  -  $(22.6 \pm 0.8) \times 10^{-8}$  einsteins  $s^{-1} cm^{-2}$ . The ratio  $R$  between the molar concentration of photoinitiator IV and that of diacrylate monomer was varied between 0.005 and 0.095.

Some typical graft yield curves of I onto cellulose in the presence of IV as the photoinitiator are reported in Fig. 1. In some cases, and particularly for  $n/S \leq 30$   $\mu mol cm^{-2}$ , where  $n$  is the number of moles of monomer initially deposited per unit apparent surface  $S$  of cellulose, a single constant-rate process was observed. With  $n/S > 30$   $\mu mol cm^{-2}$ , a very brief induction period followed, which sometimes could not even be detected experimentally, and then there was a second constant-rate process up to high graft yields, corresponding to a nearly complete reaction of the amount of diacrylate monomer initially present.

A significant parameter for the photografting processes is the moles of monomer grafted per unit apparent surface at the end of the first constant-

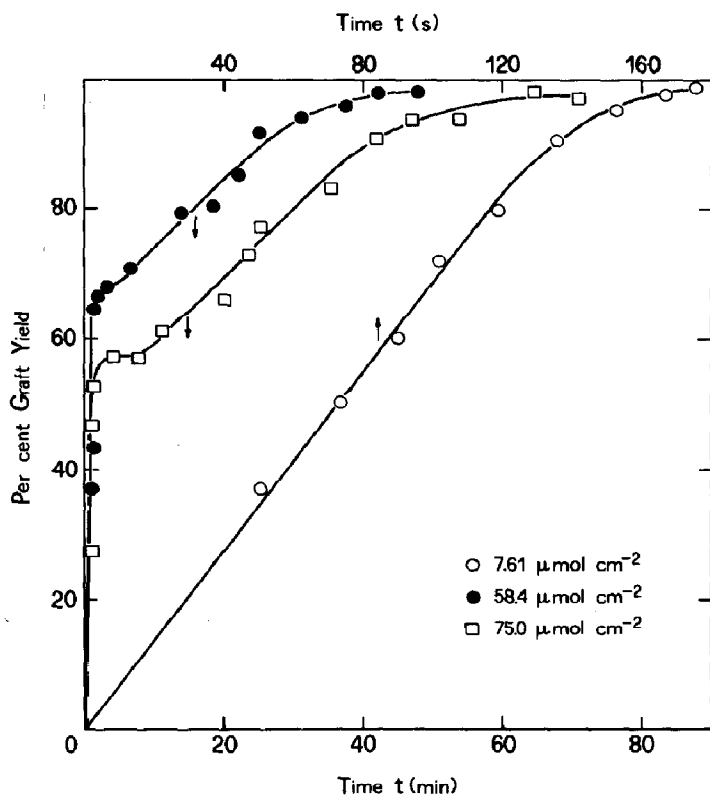


Fig. 1. Some examples of the influence of  $n/S$  (moles of monomer deposited per unit apparent surface of cellulose) on per cent graft yield as a function of irradiation time, for 1,6-hexanediol diacrylate at  $R = 0.046$  and with an irradiation flux of  $(16.5 \pm 0.6) \times 10^{-8}$  einsteins  $\text{s}^{-1} \text{cm}^{-2}$ .

rate period. In Fig. 2 this parameter is reported as per cent graft yield and plotted as a function of the initial  $n/S$  values of monomers I - III adsorbed onto the cellulose, and at various values of  $R$  above 0.025. The following experimental findings were obtained.

(i) For  $n/S \leq 30 \mu\text{mol cm}^{-2}$  a graft yield above 95% has already been reached by grafting; this is the reason why the second constant-rate process cannot be detected in this case.

(ii) No influence of the photoinitiator concentration on the graft yield measured at the end of the first constant-rate period could be detected for  $R$  between 0.025 and 0.095.

(iii) This parameter did not appear to be sensitive to the small chemical differences between the various diacrylate monomers I - III tested.

The influence of  $R$  on this parameter is illustrated in Fig. 3 for various initial  $n/S$ : a plateau is reached for  $R > 0.025$  and is maintained up to the highest value of  $R$  investigated in this work.

The two constant-rate periods, even at different energies of irradiation, could be interpreted and rationalized by the photochemical rate equation

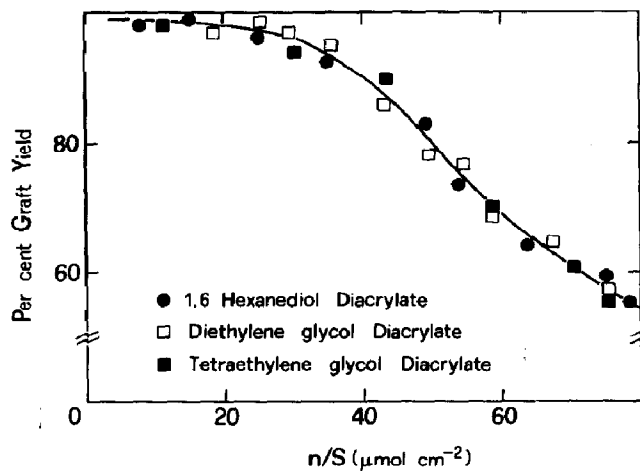


Fig. 2. Per cent graft yield measured at the end of the first constant-rate period as a function of  $n/S$  (moles of monomer deposited per unit apparent cellulose surface) for monomers I - III at various values of  $R$  (the ratio between molar concentration of photoinitiator and monomer) ranging from 0.025 to 0.095.

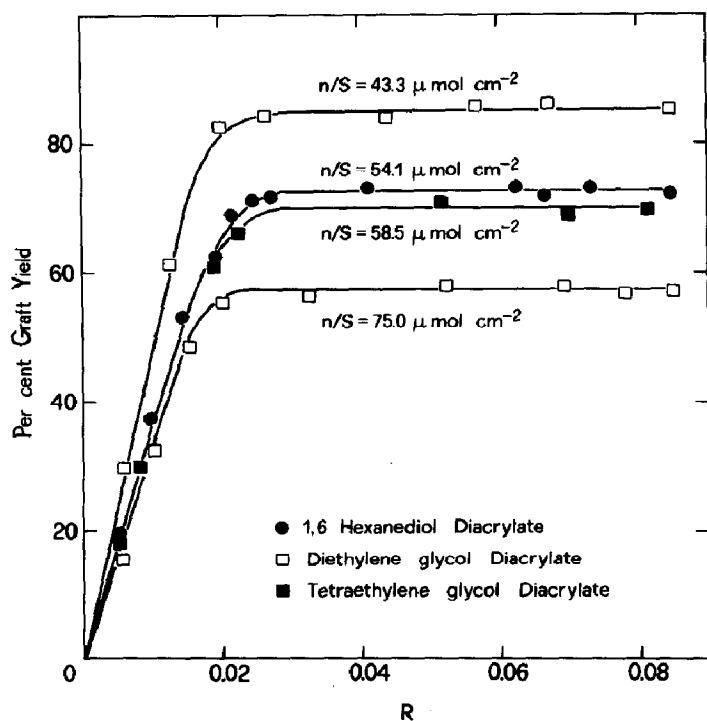


Fig. 3. Some examples of the influence of  $R$  (ratio between molar concentration of photoinitiator IV and that of monomers I - III) on per cent graft yield measured at the end of the first constant-rate period, at various  $n/S$ . (Irradiation flux,  $(16.5 \pm 0.6) \times 10^{-8}$  einsteins  $\text{s}^{-1} \text{cm}^{-2}$ .)

$$\frac{1}{S} \frac{dn}{dt} = \Phi_{1,2} I \quad (1)$$

where  $n$  is the number of moles of diacrylate monomer per apparent surface  $S$  ( $\text{cm}^2$ ) of cellulose present at time  $t$  (s),  $\Phi_{1,2}$  ( $\text{mol einstein}^{-1}$ ) is the mean polychromatic quantum yield of the first (subscript 1) or second (subscript 2) process and  $I$  ( $\text{einsteins s}^{-1} \text{cm}^{-2}$ ) is the radiation flux effectively absorbed by the sample. Within each constant-rate period, the left-hand side of eqn. (1) could be evaluated by linear regression analysis of the experimental data for the various values of incident radiation flux. The quantum yields  $\Phi_{1,2}$  could thus be evaluated. As the absorptivities of the photochemically reacting mixture and the quantum yields are wavelength dependent, integral values were used over the absorption spectrum of the mixture and emission spectrum of the lamp.

The quantum efficiencies  $\Phi_1$  were found to be practically independent of both the kind of diacrylate monomer I - III and the  $n/S$ , at least to within the limit of experimental error; this indicates that concentration quenching is not efficient or is not detectable at all, probably because of the very low value of the quenching rate constant, which may be assumed to be equal to the diffusion-controlled rate constant in the very viscous reacting medium, as well as by reason of the high  $\Phi_1$  measured under the experimental conditions. In contrast,  $R$  was observed to have a marked effect. For all tested monomers, by linear regression analysis of the experimental data, the following correlation could be ascertained:

$$\Phi_1 = (5.3 \pm 0.4) \times 10^2 R \quad (2)$$

The  $\Phi_2$  values, on the contrary, were independent of the relative concentration of the photoinitiator IV expressed by the ratio  $R$ , but they were sensitive, even if only in an unclear manner just outside the experimental uncertainty, to the very slight differences in chemical structure between monomers I - III. The more noticeable dependence of  $\Phi_2$  on  $n/S$  resulted in a good linear correlation between  $\Phi_2^{-1}$  and  $n/S$  whose slope is indicative of the very moderate influence of the monomer structure: for monomer I

$$\Phi_2^{-1} = (1.05 \pm 0.08) + (5.4 \pm 0.2) \times 10^3 n/S$$

For monomer II

$$\Phi_2^{-1} = (0.98 \pm 0.09) + (4.3 \pm 0.3) \times 10^3 n/S$$

and for monomer III

$$\Phi_2^{-1} = (0.94 \pm 0.07) + (4.8 \pm 0.2) \times 10^3 n/S$$

where  $n/S$  is in moles per centimetre squared of unit apparent surface.

All the photochemical parameters qualitatively confirm the reaction scheme proposed in ref. 21 for grafting of acryloxy-substituted aromatic diazenes onto various polymeric substrates. The high and technologically significant quantum efficiency reached when using large amounts of bi-

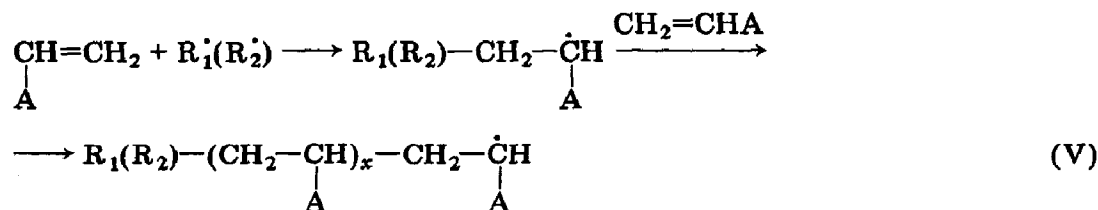
functional monomers in a viscous medium allowed detailed quantitative information to be gained on the mechanism, and this is true of the present work.

The photochemical events which initiate the process presumably consist either in a photoinitiator-radical-induced hydrogen abstraction from the reactive sites of the cellulose surface (reaction (III)), or in a photoinitiator-sensitized glucosidic bond scission (reaction (IV)) via energy transfer from the photoinitiator triplet state [26].



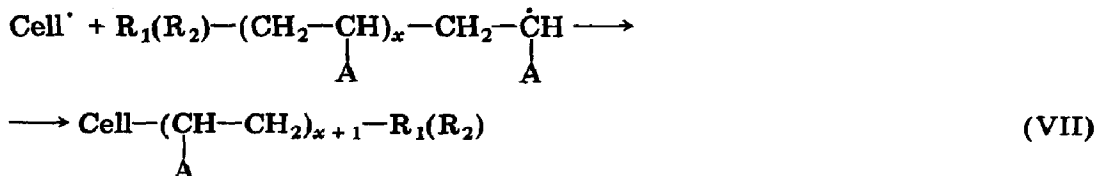
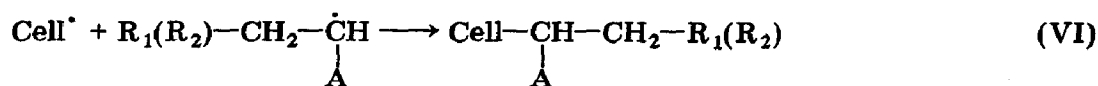
(Cell, cellulose;  $R_1$ ,  $C_6H_5C=O$ ;  $R_2$ ,  $C_6H_5C(OMe)_2$ ;  $R_1R_2$ , photoinitiator)

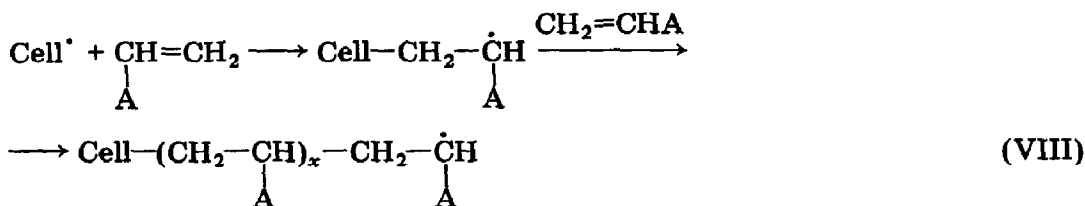
Photochemically produced radical fragments from the initiator, moreover, initiate homogeneous-phase polymerization:



(A,  $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-(\text{CH}_2)_6-\text{O}-\text{CO}-$  for I and similarly for II and III;  
 $x$ , integer)

The grafting mechanism may proceed following two parallel reaction pathways: (i) grafting of a "monomolecular layer" of acrylated monomer (reaction (VI)); (ii) grafting of an oligomolecular layer of homopolymer formed either by photoinitiator radical propagation (reaction (VII)) or by cellulose radical propagation (reaction (VIII)).





Under the experimental conditions of the present study the very high values of  $\Phi_1$  and their strong dependence on  $R$  (eqn. (2)) suggest that the prevailing reaction should be grafting of growing oligomeric chains onto the substrate.

As to the second constant-rate period, the experimental finding of an induction time after the first grafting period, no matter how brief, suggests that the reactions which predominate in the second stage are different from those involved in the first stage. Otherwise a smooth curvature would be observed in the transition between the two processes, rather than a sharp variation in slope preceded by an induction phenomenon. Similar behaviour discovered in other instances [17 - 24] has been interpreted as surface deactivation [17, 21]. Moreover, the independence of  $\Phi_2$  from the photoinitiator concentration rules out the possibility that the photoinitiator acts as a radical producer in the second stage (reaction (II)).

Among the possible hypotheses, two appear worthy of consideration: either radical formation from residual monomer molecules, possibly via energy transfer by photoinitiator triplets [26] or a similar process involving the pendant acrylate groups of the grafted chains. Both these reactions should lead to a step-by-step graft polymerization onto the first grafted layer [21], which is not inconsistent with a limiting unitary quantum yield  $\Phi_2$  as  $n/S$  tends to zero, which is independent of photoinitiator concentration as observed experimentally. However, it is not possible to choose between these two hypotheses just on the basis of the experimental data obtained by gravimetric analysis of grafting for the two constant-rate periods.

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