PHOTOSYNTHETIC MEMBRANES
IV: KINETIC INVESTIGATION OF PHOTOINITIATED GRAFTING AND PHOTO-CROSS-LINKING OF AN EPOXYDIACRYLATE RESIN ONTO CELLULOSE

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Summary

Photochemical grafting onto cellulose and successive photo-cross-linking of 2.00 - 37.00 mg cm^{-2} of an epoxydiacrylate prepolymer based on glycidyl ether of bisphenol A, containing 25 wt./wt.% trimethylolpropane triacrylate, were investigated kinetically at 30 °C in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as a photoinitiator, with the weight concentration ratio of photoinitiator to prepolymer varied between 0.070 and 1.115. Irradiations were carried out polychromatically, in air or under a stream of nitrogen, with incident radiation of flux I ranging from 2.1×10^{-8} to 20.5×10^{-8} einsteins s^{-1} cm^{-2}. Graft yields as a function of irradiation time were determined gravimetrically: two consecutive kinetic processes were observed which had rates linearly dependent on I. The quantum yields Φ_1 of the first constant-rate period showed a linear dependence on photoinitiator concentration, while the quantum yields Φ_2 for the second constant-rate process showed an inverse dependence on n/S (moles of prepolymer initially deposited per unit apparent cellulose surface). Kinetic analysis of the degree of unsaturation by multiple internal reflection IR spectroscopy was carried out in parallel and the results indicated that a structure with one pendant acrylate group per monomer unit may be assigned to the grafted polymer. At longer irradiation times, further decrease in unsaturation resulting from photo-cross-linking was observed which had a rate linearly dependent on $I^{0.5}$, suggesting a bimolecular termination for this process. In the light of this information, the mechanism of photografting of polyfunctional acrylate monomers onto polymeric surfaces is discussed.

1. Introduction

The interesting physical properties of epoxyacrylates (*e.g.* their low sensitivity to weathering and to chemical attack, their excellent surface

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hardness and their impact resistance characteristics [1]) make them particularly attractive in radiation-curable systems. Laser-induced polymerization of these materials has been recently studied [2] and was shown to be promising for the production of microelectronic components by direct drawing of the printed circuit by the laser beam. Photografting of epoxyacrylates onto poly(vinyl chloride) has also been investigated [3]. During the course of our experiments to prepare membranes suitable for gas—gas or liquid—liquid separations by photochemical grafting and graft polymerization, we first examined monoacrylated and diacrylated monomers [4 - 6], by studying the kinetics of these processes as well as the transport properties of the photosynthetic layers, in order to gain preliminary mechanistic information.

In the present paper, we have extended our investigations to an epoxydiacrylate prepolymer blended with a triacrylate monomer, both to obtain higher photochemical rates than those achieved using diacrylates [7] and to consider in detail the influence of irradiation on photo-cross-linking in this system.

2. Experimental details

Cellulose in the form of filter paper ("black band", Schleicher and Schüll, F.R.G.) was employed as the substrate. A commercial epoxydiacrylate resin was used (Ebecryl 616 from UCB, Belgium) which consisted of a mixture containing 75 wt./wt.% of a low molecular weight diacrylate prepolymer derived from glycidyl ether of bisphenol A, and 25 wt./wt.% trimethylolpropane triacrylate as a reactive diluent. The mean molecular weight of the prepolymer mixture was 5.0×10^2. 1,2-Diphenyl-2,2-dimethoxyethanone (Fratelli Lamberti, Italy) was the photoinitiator, and this was used as received without further purification.

1 - 2 ml of a solution of dry dichloromethane containing 56.55 - 523.1 g l^{-1} Ebecryl 616, and photoinitiator with the ratio R_w (its weight concentration with respect to that of the prepolymer mixture, corresponding to the molar ratio R if calculated from the mean molecular weight of the prepolymer) varied between 0.070 and 0.115, was uniformly deposited by a standard procedure, described previously [5], on a cellulose disk 6 cm in diameter. After evaporation of the solvent under vacuum at room temperature, irradiation and gravimetric determination of the graft yields as a function of irradiation time were performed as described in ref. 5, with the only difference being that Soxhlet extraction for the removal of non-reacted monomer or prepolymer and ungrafted homocopolymers was carried out with dichloromethane as the solvent.

Analysis of residual unsaturation was carried out as a function of irradiation time by multiple internal reflection IR spectroscopy using the technique described in ref. 6.

3. Results and discussion

Photochemical grafting of epoxydiacrylate prepolymer Ebecryl 616 onto cellulose, in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as the photoinitiator, was investigated kinetically at 30 ± 2 °C. Irradiation was carried out polychromatically with incident radiation fluxes in the range $(2.1 \pm 0.2) \times 10^{-8}$ - $(20.5 \pm 0.8) \times 10^{-8}$ einsteins s^{-1} cm^{-2}, by operating either under a stream of nitrogen or in air. The mass m of epoxydiacrylate prepolymer adsorbed per unit apparent surface S of cellulose was varied between 2.00 and 37.00 mg cm^{-2}; the ratio R_w of the weight per cent of photoinitiator to that of prepolymer was varied between 0.070 and 1.115. Graft yields as a function of irradiation time were determined gravimetrically. Kinetic analysis of unsaturation was also carried out in parallel. Some typical experimental curves are reported in Figs. 1 and 2. In some cases, and particularly for $m/S \leqslant 17$ mg cm^{-2}, only a single constant-rate process was observed (e.g. see Fig. 1). With $m/S > 17$ mg cm^{-2}, a second constant-rate process, of much lower rate, followed up to high graft yields, as determined gravimetrically (e.g. see Fig. 2). In each case, the rates in air were relatively low compared with those obtained when irradiation was effected under a stream of nitrogen (it is well known that oxygen inhibits polymerizations proceeding by a free-radical mechanism).
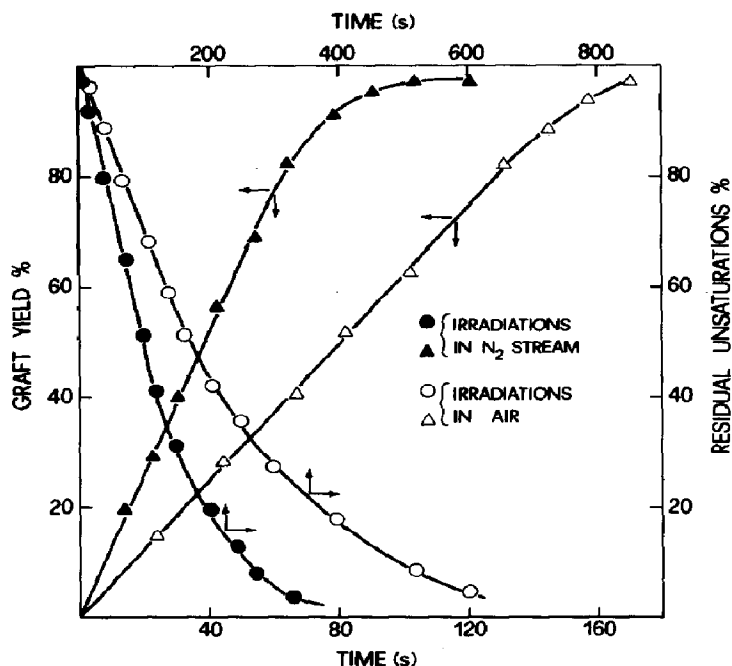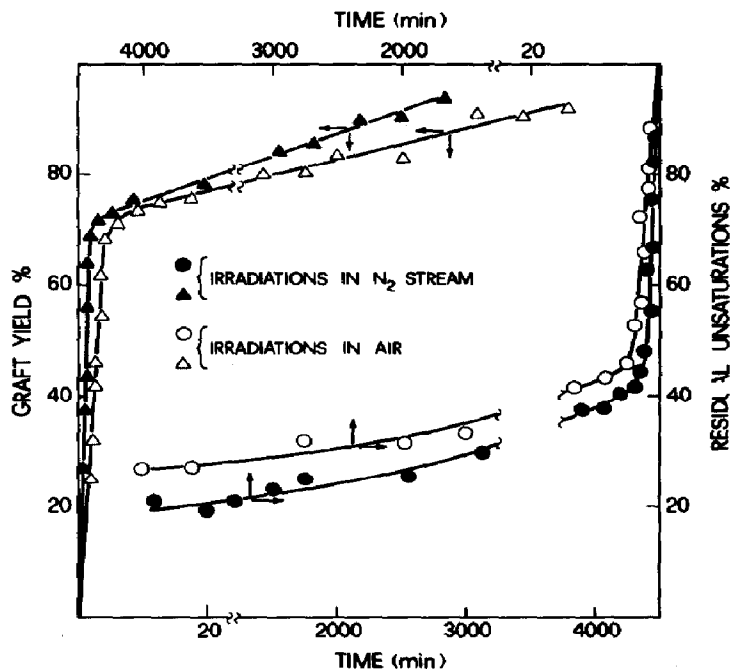

Fig. 1. Per cent graft yield (gravimetric analysis) and per cent residual unsaturation (acrylate functions, by multiple internal reflection IR spectroscopic analysis) of 7.49 mg cm^{-2} diacrylate prepolymer Ebecryl 616 onto cellulose, as a function of irradiation time t, in the presence of 7 wt./wt.% 1,2-diphenyl-2,2-dimethoxyethanone as the photoinitiator (irradiation flux, $(13.8 \pm 0.6) \times 10^{-8}$ einsteins s^{-1} cm^{-2}). Irradiations were carried out either under a stream of nitrogen or in air.

Fig. 2. Per cent graft yield (gravimetric analysis) and per cent residual unsaturation (acrylate functions, by multiple internal reflection IR spectroscopic analysis) of 35.0 mg cm^{-2} diacrylate prepolymer Ebecryl 616 onto cellulose, as a function of irradiation time t, in the presence of 7 wt./wt.% 1,2-diphenyl-2,2-dimethoxyethanone as the photoinitiator (irradiation flux, $(20.5 \pm 0.7) \times 10^{-8}$ einsteins s^{-1} cm^{-2}). Irradiations were carried out either under a stream of nitrogen or in air.
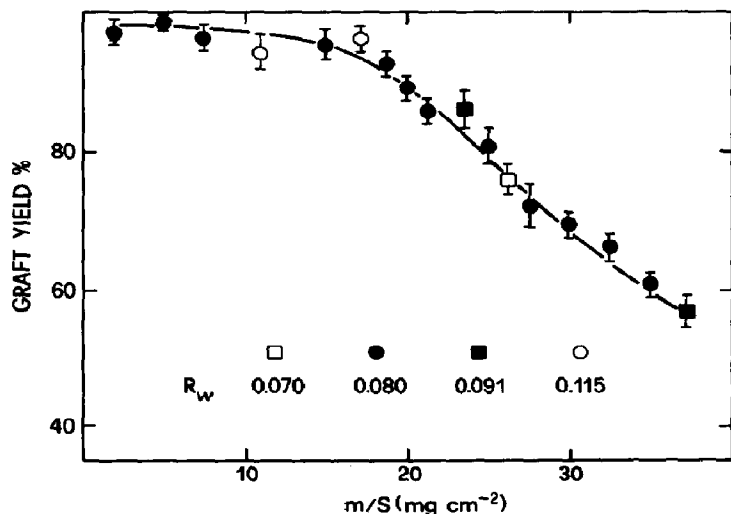

Fig. 3. Per cent graft yield (gravimetric analysis) measured at the end of first constant-rate period as a function of m/S (mass of prepolymer Ebecryl 616 deposited per unit apparent surface of cellulose) at various values of R_w (ratio of the weight per cent of 1,2-diphenyl-2,2-dimethoxyethanone to that of the prepolymer) and various irradiation fluxes ranging from 2.1×10^{-8} to 20.5×10^{-8} einsteins s^{-1} cm^{-2}. (Irradiations were carried out under a stream of nitrogen.)

As in the kinetic examination of photoinitiated grafting of diacrylate monomers [5], the mass of monomer grafted per unit apparent surface at the end of the first constant-rate period is an important parameter. In Fig. 3 this parameter is reported as per cent graft yield as a function of the initial m/S of prepolymer adsorbed onto cellulose, at various values of R_w. Both the occurrence of a single-rate process for initial $m/S \leqslant 17$ mg cm^{-2} and the absence of any influence of the photoinitiator concentration on the graft yield measured at the end of the first constant-rate period can be clearly observed, at least in the range of R_w tested.

The experimental data for the two constant-rate periods, even at different energies of irradiation, can be interpreted by the photochemical rate equation

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

where n is the number of moles of prepolymer (calculated from their mass using the mean molecular weight of 5.0×10^2), S (cm^2) is the apparent surface of cellulose, t (s) is the time, $\Phi_{1,2}$ (mol einstein^{-1}) is the mean polychromatic quantum yield of the first (1) and second (2) constant-rate processes, as determined from gravimetric measurements of the graft yield and I (einsteins s^{-1} cm^{-2}) is the radiation flux effectively absorbed by the sample. The data can be fitted quite satisfactorily to this equation. $\Phi_{1,2}$ can thus be evaluated, as described previously [5].

The resulting Φ_1 show a linear correlation with R (the ratio of the molar concentration of the photoinitiator to that of the prepolymer, calculated from the mean molecular weight) and are practically independent of the initial n/S, at least within the limits of experimental uncertainty. The equations

$$\Phi_1 = (4.0 \pm 0.4) \times 10^4 R \qquad \text{for a nitrogen stream} \qquad (2a)$$

$$\Phi_1 = (1.9 \pm 0.2) \times 10^4 R \qquad \text{for air} \qquad (2b)$$

adequately represent the experimental data. The very high value of the slope of Φ_1 *versus* R, about 75 times greater than that observed with diacrylate monomers [5] when irradiation was performed under an inert atmosphere, is undoubtedly due to the presence of the triacrylate monomer in the photochemically reacting mixture. At the end of this stage, when a highly crosslinked structure had already been obtained from the investigated prepolymer, a marked decrease in rate was noticed. This may be due both to the phase variation of the surface layer, which changed from an adsorbed viscous liquid into a solid grafted phase, and to the fact that residual acrylate functions of the polymer chain, as well as non-reacted monomer molecules (if excess monomer was present), remained entrapped in the grafted polymer structure.

During the second constant-rate process, the photoreactions of the double bonds continued to show a linear dependence of rate on radiation

intensity. However, by contrast with the first constant-rate stage, no dependence of quantum efficiency on photoinitiator concentration was observed.

The quantum yields Φ_2 were moderately dependent on the n/S, with a good linear correlation between Φ_2^{-1} and n/S:

$$\Phi_2^{-1} = (0.93 \pm 0.08) + \frac{(6.9 \pm 0.3) \times 10^3 n}{S} \tag{3a}$$

under a stream of nitrogen and

$$\Phi_2^{-1} = (1.07 \pm 0.08) + \frac{(9.8 \pm 0.7) \times 10^3 n}{S} \tag{3b}$$

in air, where n/S is expressed in moles per square centimetre.

The quantum yields Φ_1 and Φ_2 calculated from eqn. (1) using experimental data obtained from gravimetric analysis were identical with those obtained from the residual acrylate functions determined by multiple internal reflection IR analysis, provided that one out of two acrylate functions of the epoxydiacrylate compound derived from the glycidyl ether of bisphenol A was considered as grafted, and two out of three acrylate functions of trimethylolpropane triacrylate were similarly considered as grafted. This is perfectly consistent with the result previously found [6] that a structure with one pendant acrylate group per monomer unit may be assigned to the grafted polymer.

Further irradiation of the grafted polymer, for which a practically quantitative graft yield, as determined gravimetrically, had already been reached, reduced the residual unsaturation as illustrated in Fig. 2. In this way an even more highly cross-linked polymer could be obtained. The experimental rates r_c of photo-cross-linking, calculated at various incident radiation fluxes, are shown in Fig. 4. A linear correlation of r_c with $I^{0.5}$ (Fig. 4) best typifies the experimental behaviour. It may be inferred that, at least in the range of irradiation fluxes and photoinitiator concentrations used in the present work, photo-cross-linking of residual pendant acrylate groups follows a classic bimolecular termination mechanism, as required by the linear dependence of r_c on $I^{0.5}$.

The experimental data obtained in this work agree satisfactorily well with the reaction mechanism [5] proposed for grafting of diacrylate monomers onto cellulose, when the first and second constant-rate grafting periods, following eqn. (1), are considered. This mechanism implies photochemical reactivity of one out of two acrylate functions during the first constant-rate period and may be easily extended to grafting of trifunctional acrylates provided that two out of three acrylate groups are considered to react; in this case a greater quantum efficiency may be observed and a consequently higher cross-linking in the polymer network.

As to the second constant-rate period, two possible reaction mechanisms have been hypothesized [5]: (i) radical formation from monomer molecules remaining at the end of the first stage, via energy transfer by photoinitiator triplets; (ii) a similar photoactivated process involving pendant
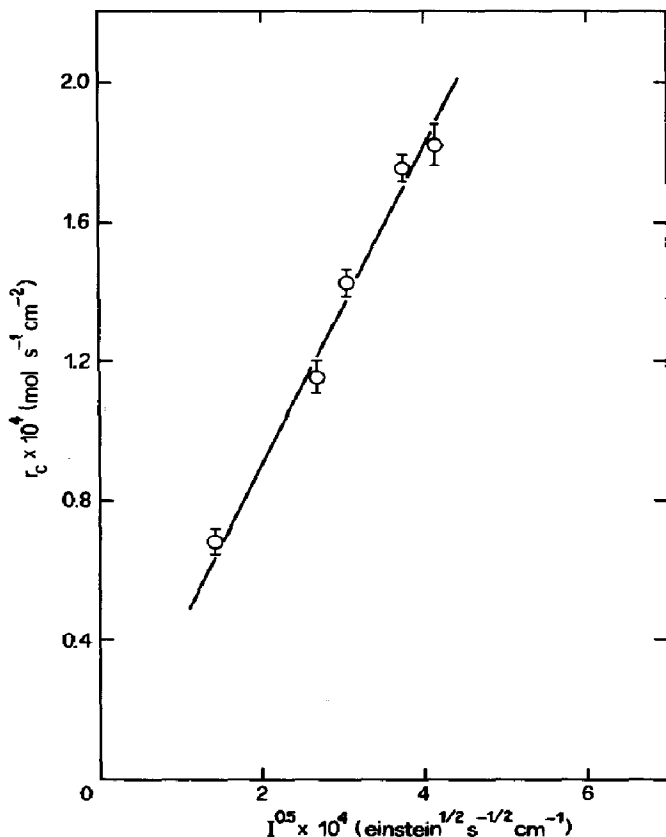
Fig. 4. Rate r_c of photo-cross-linking (in moles of acrylate functions per square centimetre per second), as measured at the end of the photografting period by multiple internal reflection IR spectroscopic analysis, as a function of the square root of the absorbed radiation intensity $I^{0.5}$ per unit apparent cellulose surface, for 8.65 mg cm^{-2} epoxydiacrylate prepolymer Ebecryl 616, in the presence of 0.080 wt./wt.% photoinitiator. (Irradiations were carried out under a stream of nitrogen.)

acrylate groups of grafted chains. Information obtained in this work from kinetic analysis of unsaturation, and particularly the dependence of the photo-cross-linking rate on the square root of the radiation intensity after the end of the second constant-rate period, suggests that hypothesis (i) should be favoured, probably because of a higher rate of radical formation from residual free monomer molecules than from less mobile pendant acrylate groups. The latter react with a slower rate which is not linearly dependent on the radiation intensity; the reaction, detectable only when the grafting process is practically complete, leads to photo-cross-linking between reactive sites of grafted chains and consequently to a modification of the transport properties of the grafted layer [6].

Acknowledgments

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