STUDY OF METHACRYLAMIDE GRAFTING ONTO CELLULOSE TRIACETATE FILMS UNDER ULTRAVIOLET LIGHT*

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AN EARLIER investigation [1] of the grafting of methacrylamide onto the surface of cellulose triacetate films using UV irradiation had shown that the grafting gave rise to an insoluble graft copolymer in the form of a surface film. The study of the acidity changes of the cellulose triacetate (CTA) film during UV irradiation had led to the theory that the free radicals which initiate the grafting are created at the points of acyl radical dissociation.

The formation of free radicals in CTA could also take place on glucoside bond fracture or the liberation of an α-hydrogen atom from the main chain. Glucoside chain fracture in CTA can be detected with UV absorption at 2480 Å and below [2]. The same fracture, but in the cellulose molecule, takes place at 2537 [3] or 2660 Å [4, 5].

The aim of this work was to determine the wavelength of the UV light which would lead to the formation of sufficiently reactive free radicals to initiate the graft copolymerization of methacrylamide with the surface of CTA films.

EXPERIMENAL

CTA with a bound acetic acid content of 61·9% was used to prepare 0·1 mm thick films by pouring its solution in 9 : 1 methylene dichloride and methanol on to the surface of mirror glass. Formation of the film from solution and its drying were carried out in a nitrogen atmosphere. A 9% concentration of benzophenone on TCA was used in the solution as the photo-sensitizer.

The films were irradiated with UV light in the presence of the methacrylamide (MAA) solution using a Tesla Tube TNK-700 on an assembly described earlier [1]. An optical filter consisting of a number of films of the same composition as that subjected to grafting was placed between the TCA film and the light source. By varying the thickness of this one could alter the total thickness of the filter and thus also the spectral composition of the radiation.

A uranyl oxalate actinometer was placed together with the film under test in the chamber filled with nitrogen. The irradiated film was removed from the chamber, washed with distilled water and left for 16 hr in water at 40°C to remove any homopolymer (MAA). The film was then dried for 1 hr at 90°C and left for 24 hr in a 9 : 1 mixture of methylene dichloride with methanol to remove the uncopolymerized CTA. The solution was prepared

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in both cases by mixing with a magnetic stirrer. The insoluble graft copolymer which remained was dried to constant weight and the weight per unit of irradiated surface of the original film was determined.

Titration of the actinometric solution by the usual method [6] gave the irradiation intensity per unit surface area of the filter. Confirmation of the dependence of grafting on irradiation intensity was obtained by using the same apparatus and method, but different types of filter. The optical filter was in this work placed between the light source and the sample, and also between the light source and the actinometer, i.e. the irradiation intensity was measured directly.

RESULTS

Preliminary experiments had confirmed the theory that the amount of graft copolymer, P, was proportional to the square root of UV light intensity:

$$P = A \cdot \sqrt{I_{irrad}}. \tag{1}$$

Where the UV light was filtered first, its intensity at the surface of the film would obey the Lambert–Beer rule according to:

$$I_{irrad} = I_0 \cdot e^{-k_\lambda d}, \tag{2}$$

in which I_0 is the intensity of UV light before filtering, d—thickness of the filter.

By combining equations (1) and (2), using the derivation $A \cdot \sqrt{I_0} = B$, one gets

$$P = B \cdot e^{-k_\lambda d/2} \tag{3}$$

which, transformed into logarithms, gives finally

$$\log P = \log B - (k_\lambda / 4{\cdot}606) \cdot d \tag{4}$$

The plotting of grafting as a function of thickness of the filtering film will thus be a straight line.

The experimental results (Fig. 1) fully confirmed this theory. The slope of this line is, according to equation (4), proportional to the extinction coefficient of the filter for the wavelength of the UV light. A more exact determination of

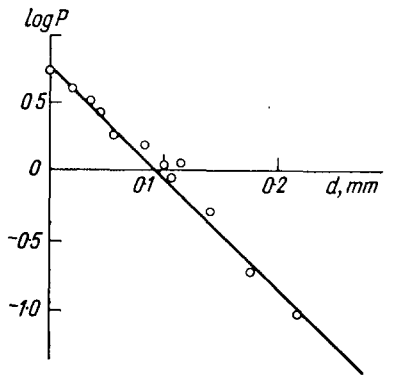

FIG. 1. Grafting as a function of the thickness of the filtering layer.