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THE EFFECT OF VISIBLE AND NEAR-UV RADIATION ON PREHEATED CELLULOSE: A PHOTOCHROMIC PHENOMENON

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Summary

Preheated cellulose was irradiated with UV and visible light ($\lambda_{exc} >$ 290 nm). Measurements of the diffuse reflectance factors lead to the determination of the relative changes in the effective cross section for absorption and diffusion. The depth of penetration of the incident beam was also studied. Irradiation with near-monochromatic light produced a decoloration exactly centred at the excitation wavelength. The relative quantum yields of decoloration were found to decrease with exposure time but to be independent of λ_{exc}. The observed behaviour is interpreted assuming the presence of a set of chromophores belonging to a homologous family.

1. Introduction

The modes of action of UV and visible light on cellulose have been the object of a large number of studies in the contexts of both direct and photosensitized irradiation. Baugh's recent review [1] summarizes this abundant literature. One is readily made aware of the apparent contradictions among results and conclusions published by different authors which, however, mostly arise from the complexity of the phenomena examined and the difficulties of reproducing the experimental conditions of a given type of investigation. Thus, even minor changes in the chemical and/or physical characteristics of the samples, as well as in the wavelength of excitation or the temperature, can induce important phenomenological changes.

The photochemical degradation of cellulosic materials is a surface event [2] which produces a yellowing of the samples and the appearance of free-radical species [3], the extent of these effects being particularly pronounced at $\lambda_{exc} < 280$ nm. Traces of lignine accelerate the degradation, probably through photosensitization. At longer wavelengths the opposite effect is often noticed in that yellowed materials are bleached by the irradiation [4 - 6]. Launer [6] studied qualitatively the photobleaching of various types of cellulosic specimens and found that a "spectral conformity" existed between the irradiation wavelength and the maximum in the diffuse reflectance spectrum of the bleached sample.

None of the mechanisms of photodegradation proposed thus far seems thoroughly satisfactory in terms of explaining the complex set of features observed, even on a qualitative basis. Already the precise origin of the absorption (which is not due to any of the structural groups which make up the normal cellulosic chains) is uncertain, and can only be attributed tentatively to "impurities" or "faults" bearing carbonyl and/or carboxyl groups [7]. This complicated situation has led to some research on model compounds in order to simulate the photolysis of cellulose in a simplified and more controllable fashion [8]. This approach, however, as with similar work dealing with synthetic polymers, can be misleading since the extrapolation of results obtained with small model molecules to the behaviour of macromolecules is always risky and often totally unjustified because the initiation pathways with polymeric substrates originate mostly at structural imperfections (e.g. double bonds, head-to-head sequences and oxidized sites) and therefore bear little relation to the actual stability of the normal sequence of monomer units, i.e. with model compounds.

We have been interested in the effect of UV and visible radiation upon ligno-cellulosic materials [9 - 12]. In our studies with "pure" cellulose, in which we used diffusion spectrophotometry, the existence of two separate domains of photochemical behaviour was shown: (i) irradiation at $\lambda_{exc} <$ 300 nm produced a yellowing of the substrate and a weight loss due to the formation of volatile photoproducts [9], while (ii) irradiation at $\lambda_{exc} >$ 300 nm led to bleaching without any weight loss following a photochromic phenomenon [10]. The present communication reports more detailed work on the action of monochromatic or polychromatic light in the spectral region 300 - 700 nm on cellulose samples which have been conditioned by thermal aging. The main purpose of this study was to gain a deeper insight into the nature of the photochromic behaviour of cellulose [6, 10, 11].

2. Experimental details

2.1. The substrate and its irradiation

The strips to be tested were cut from a paper sheet 59 μm thick (30 g m^{-2}) made with BX-50 regenerated cellulose, i.e. extremely pure cellulose fibres. These strips were aged artificially in a ventilated oven kept at 120 ± 0.2 °C for 48 h (heat treatment "H"). They were exposed to light in a Xenotest-150 apparatus after this "conditioning" process. The source of irradiation was a 1600 W xenon arc which was used with appropriate filters to give the following types of illumination: (i) $\lambda_{exc} >$ 290 nm; (ii) $\lambda_{exc} >$ 300 nm; (iii) near-monochromatic excitation using Wratten gelatine filters (Kodak reference numbers in parentheses) to give 430 (98), 450 (50), 470 (45), 480 (75), 520 (61), 530 (74) and 600 (72) nm. These filters, chosen because of their good stability, displayed nevertheless a slight evolution of spectral characteristics with irradiation time. They were therefore regularly

checked before and during the tests; (iv) broad-band excitation between 300 and 392 nm using an "ultraviol" filter (λ_{max} = 360 nm).

The samples were placed on a glass plate (microscope slide) set on a black background and then covered with a thin quartz plate. The sample holders were rotated continuously around the light source in order to compensate for any possible axial asymmetry of the photon flux. The temperature inside the Xenotest was kept constant at 30 ℃ by a controlled flow of cool air. The amount of radiant energy reaching the samples was measured with a balanced Moll and Burger (Kipp) thermopile.

The experiments carried out ranged from the simple illumination of a preheated cellulose strip, to several heating–illumination cycles and to the irradiation of a stack of sheets.

2.2. Collection and processing of data

The diffuse reflectance factor R_λ was measured before and after each heat or light exposure using an Ulbricht-sphere spectrophotometer. This analysis translated any effect of irradiation or thermal aging into appropriate colouration changes in the spectral range 200 - 700 nm. The method had the additional merit of being non-destructive (both in terms of chemical and physical modifications), thus allowing a clean study of the surface reactions and their kinetics.

If spectrophotometry is applied to a relatively dense solid medium such as a sheet of paper, it is necessary to be able to separate the effects of light diffusion and absorption in order to assess correctly the specific absorption of the chromophores. The relevant parameters here are the macroscopic cross sections $\Sigma_{s\lambda}$ (cm^{-1}) for diffusion and $\Sigma_{a\lambda}$ (cm^{-1}) for absorption respectively. If $\sigma_{a\lambda}$ is the microscopic cross section relative to the interaction of photons with an absorbing chromophore and C is the molar concentration of the latter in the diffusing medium, it follows that

$$\Sigma_{a\lambda} = C\sigma_{a\lambda}$$

Likewise

$$\Sigma_{s\lambda} = C\sigma_{s\lambda}$$

for diffusion, $\sigma_{s\lambda}$ being the microscopic cross section of the structural elements making up the cellulosic texture. For a mixture of components whose individual microscopic cross section is $\sigma_{i\lambda}$ and whose concentration is C_i

$$\Sigma_\lambda = \sum_{i=1}^{m} C_i \sigma_{i\lambda}$$

in the absence of interactions among the components.

The study of light transfer in diffusing media, and more specifically the measurement of the spectral reflectance factors and of the geometrical characteristics of the substrates, allows the determination of macroscopic cross sections. This approach, however, involves serious difficulties given on the one hand the complexity of multiple diffusion phenomena in media whose structure apparently becomes random in the range of wavelengths used and on the other hand the necessity to carry out absolute measurements of reflectance factors. The approximations usually made to solve the problem of light transfer depend on the actual magnitude of the reflectance factors, the modes of simple diffusion by the particles and the geometry of illumination and observation [13]. For the present study the approach formulated by Kubelka and Munk [14] seemed most appropriate since their re-emission function

$$(K/S)_\lambda = \left\{ \frac{(1 - R_\infty)^2}{2R_\infty} \right\}_\lambda \tag{I}$$

relates directly the absorption coefficient K_λ (cm^{-1}) and the diffusion coefficient S_λ (cm^{-1}) to the intrinsic diffusion spectral reflectance factor $R_{\infty\lambda}$ of a diffusing medium sufficiently thick to be considered opaque within the precision of the measurements.

Given the actual values of spectral reflectance measured in this context, which are mostly above 0.5, the ratio $(\Sigma_a/\Sigma_s)_\lambda$ of the macroscopic cross section for absorption and diffusion is proportional to $(K/S)_\lambda$ with less than 1.5% error [13]. Furthermore, it was found experimentally that $\Sigma_{s\lambda}$ was not modified in samples irradiated between 290 and 700 nm. Indeed, R_∞ and R_0 (the diffusion reflectance factor of the samples placed against a black-body background) were measured as a function of λ_{exc} and of the thickness x of the strip, and then $\Sigma_{s\lambda}$ calculated using the expression [13]

$$\Sigma_s = -\frac{1}{3x}\left\{1 + \frac{3}{4}\left(\frac{1 - R_\infty}{1 + R_\infty}\right)^2\right\}^{-1} \frac{1 + R_\infty}{1 - R_\infty} \log \frac{R_\infty - R_0}{R_\infty(1 - R_\infty R_0)} \quad (\text{cm}^{-1}) \tag{II}$$

The values of Σ_s were found to be independent of λ_{exc} in the range quoted above within experimental error, i.e. ±4%. Changes in $(\Sigma_a/\Sigma_s)_\lambda$ could therefore be attributed essentially to corresponding variations in the absorption, whose evolution was calculated in terms of a "relative colouration number" RCN defined as

$$(\text{RCN})_\lambda = 100\left(\frac{\Sigma_{a,\,final} - \Sigma_{a,\,initial}}{\Sigma_{a,\,initial}}\right)_\lambda \tag{III}$$

Taking into account the above observations gives

$$(\text{RCN})_\lambda = 100\left\{\frac{(\Sigma_a/\Sigma_s)_{final} - (\Sigma_a/\Sigma_s)_{initial}}{(\Sigma_a/\Sigma_s)_{initial}}\right\}_\lambda$$

$$= 100\left\{\frac{(K/S)_{final} - (K/S)_{initial}}{(K/S)_{initial}}\right\}_\lambda \tag{IV}$$

Clearly, a positive value of RCN indicates an increase in absorption and vice versa.

A relative quantum yield of decolouration at a given excitation wavelength can be formulated as the ratio of RCN to the number Δn of photons absorbed by the sample for any given reaction time, *viz.*

$$\Phi_{d\lambda} = \left(\frac{RCN}{\Delta n}\right)_\lambda \tag{V}$$

The number of absorbed photons can be expressed as

$$\Delta n_\lambda = \left\{\frac{I_0}{Nhc/\lambda} \int_{t=0}^{t} (1 - R_{\infty t}) \, dt\right\}_\lambda \tag{VI}$$

where $I_{0\lambda}$ (W cm^{-2}) is the incident radiation energy density, $R_{\infty t\lambda}$ is the intrinsic diffuse reflectance factor at time t, N is Avogadro's number and h is Planck's constant.

The expression of the quantum yield of decolouration now takes the form

$$\Phi_{d\lambda} = \left\{\frac{k\,RCN}{I_0\lambda \int_{t=0}^{t} (1 - R_{\infty t}) \, dt}\right\}_\lambda \tag{VII}$$

where $k = Nhc$.

The data obtained, which are discussed below, refer therefore to *relative* quantum yields which were calculated from eqn. (VII) using an arbitrary value of unity for the constant k.

3. Results and discussion

Preliminary monochromatic irradiation tests carried out on pure cellulose showed that Σ_a/Σ_s decreased with time, while the diffusion term remained constant as already mentioned above. The relative changes in Σ_a/Σ_s were however rather small. Because of this, samples were henceforth submitted to the thermal treatment described in Section 2.1, which resulted in an increase of the absorption of the cellulose both in the visible and in the UV regions of the spectrum and thus led to a substantial amplification of the bleaching phenomenon.

3.1. Influence of light penetration

Since the photochemical events under study are linked to the diffusion of photons within the material, it seemed interesting to look into the influence of the penetration depth of the radiation using superposed cellulose strips. These experiments were carried out on stacks of nine sheets of pre-heated paper (H-cellulose) which underwent two types of irradiation. Spec-
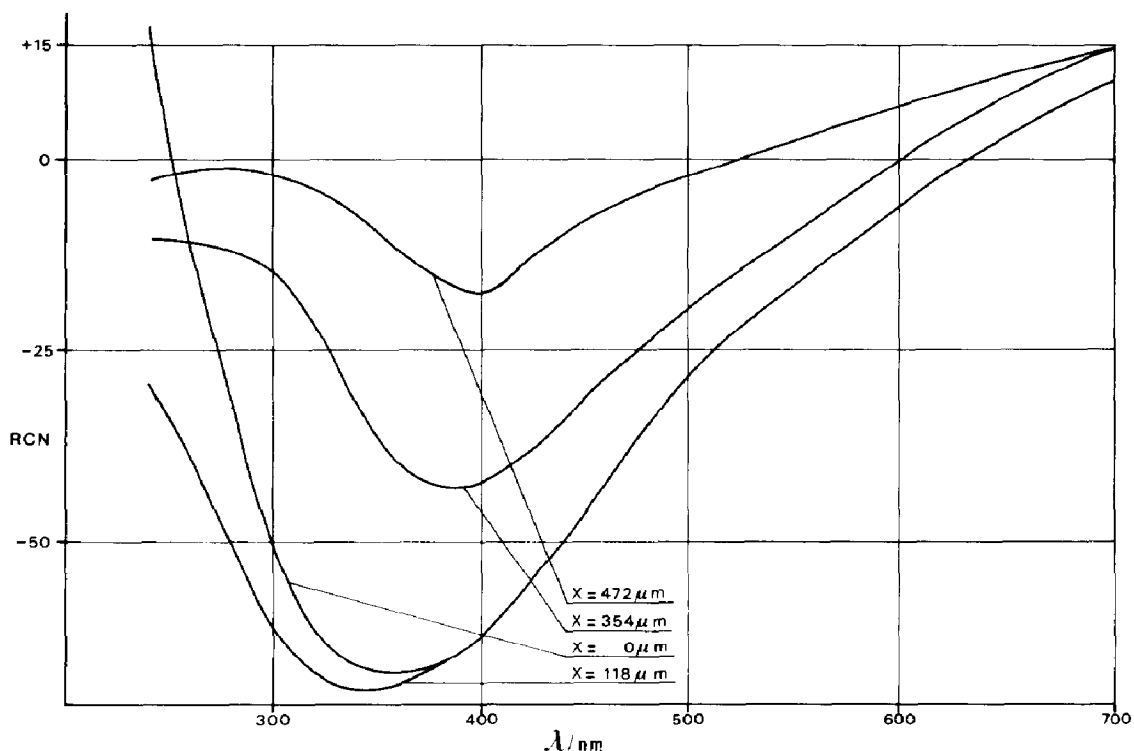
Fig. 1. Effect of the depth of penetration of radiation: RCN spectra taken at different depths x from a nine-strip stack of H-cellulose irradiated with $\lambda_{exc} > 290$ nm for 63 h.

troscopic measurements were performed on the sheets lying at the following depths from the top (illuminated face) of the stack: 0, 118, 354 and 472 μm.

With $\lambda_{exc} > 290$ nm, the RCN spectrum relative to the top sheet showed an increase of absorption in the near-UV (Fig. 1). The formation of chromophores responsible for this absorption is due to the action of the excitation wavelengths lower than 300 nm. The top sheet acts as a screen for the photons absorbed by H-cellulose and only the longer wavelengths reach the deeper layers. In contrast, radiation with wavelengths higher than 300 nm induces a decrease in both the visible and the UV absorption, as shown in Fig. 1.

With irradiation covering the excitation range 300 - 392 nm, *i.e.* using an ultraviol filter, the increase in the UV absorption of the top sheet did not take place (Fig. 2). Instead, the absorption decreased over the whole spectrum, the magnitude of this change being smaller the lower the sheet position in the stack, as in the previous experiment (except for the top sheet) (*cf.* Figs. 1 and 2).

·The following observations are relevant to these first results.

(i) With $\lambda_{exc} > 290$ nm, decolouration penetrates across the cellulosic material and the minimum in the resulting spectrum is shifted bathochromically with increasing depth as shown in Fig. 1.
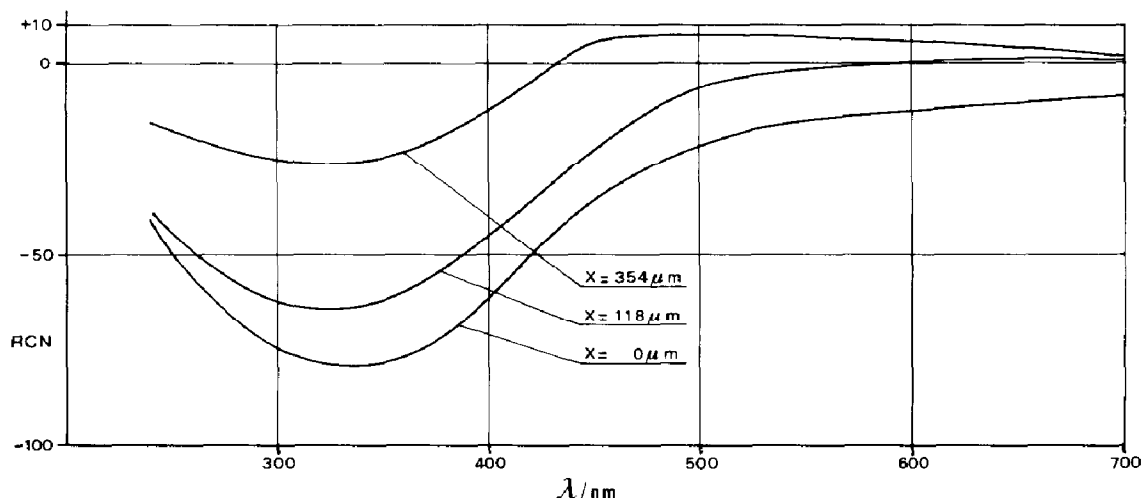
Fig. 2. Same as Fig. 1, but with irradiation covering the excitation range 300 - 392 nm filtered through an ultraviol plate (maximum transmission at 360 nm).

(ii) If irradiation is limited to the range 300 - 392 nm, the minimum in the spectra of the bleached layers is independent of the depth and coincides with the maximum transmission of the filter (*i.e.* 360 nm) as suggested by the results shown in Fig. 2.

3.2. The influence of the excitation wavelength

Figure 3 gives the RCN spectra of H-cellulose sheets irradiated at various wavelengths for 157 h. The general trend is unambiguous, showing a decrease in absorption cross section during exposure to monochromatic light which produces a wide decolouration band centred at wavelengths remarkably close to λ_{exc}. To the eye, the paper strips acquire the colour of the irradiation beam used. An excellent agreement was found between λ_{exc} and λ_a (the wavelength at which Σ_a is at a maximum) as shown in Fig. 4. A linear regression calculation gave

$$\lambda_a = (0.997 \pm 0.02)\lambda_{exc} + (0.07 \pm 9.68)$$

with a correlation coefficient of 0.9988 and a mean standard deviation for λ_a of ± 3.8 nm.

These results suggest the presence in H-cellulose of a "family" of absorbing centres, *viz.* chromophores characterized by absorption bands which partly overlap. The irradiation of the material with a given λ_{exc} induces the selective disappearance of the chromophores whose absorption maxima are centred at the irradiation wavelength, but also the partial bleaching of those possessing a weaker absorption cross section at this wavelength. The occurrence of energy transfer could also be envisaged to explain the broadness of the RCN spectra.

For the sake of comparison, Fig. 3 also shows the RCN spectrum of a strip of H-cellulose exposed to $\lambda_{exc} > 300$ nm for 157 h. This spectrum again
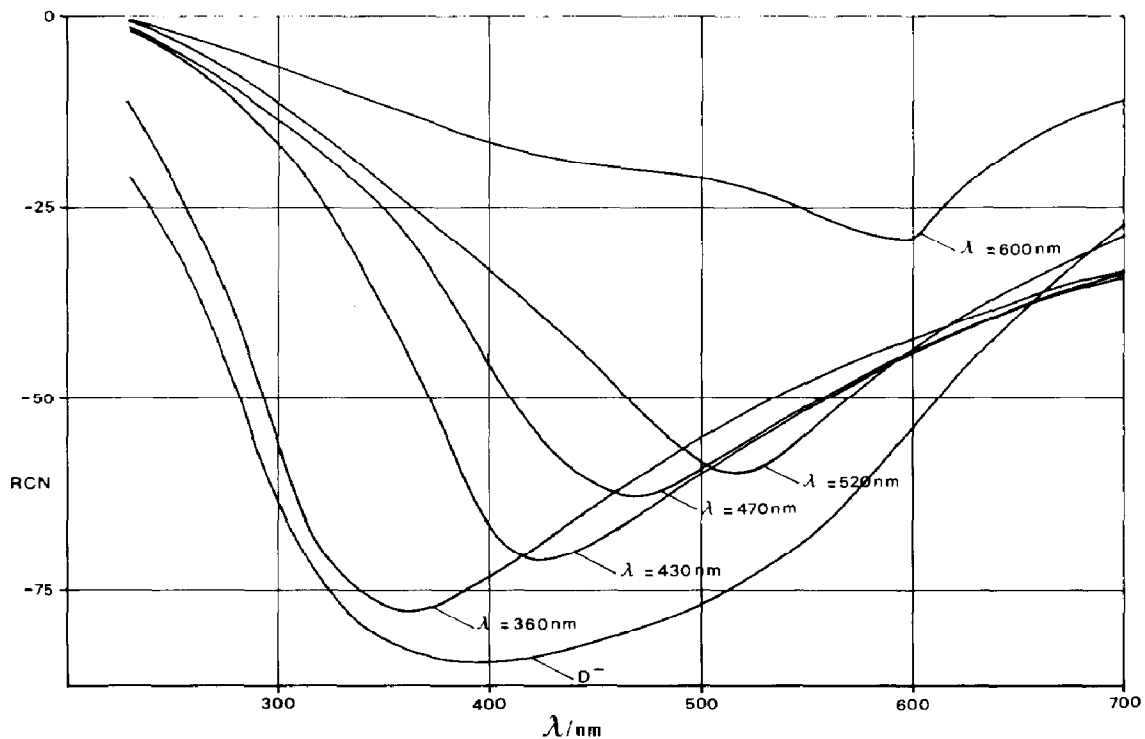
Fig. 3. Selective decolouration of H-cellulose strips using monochromatic irradiation or D^- light ($\lambda_{exc} > 300$ nm).
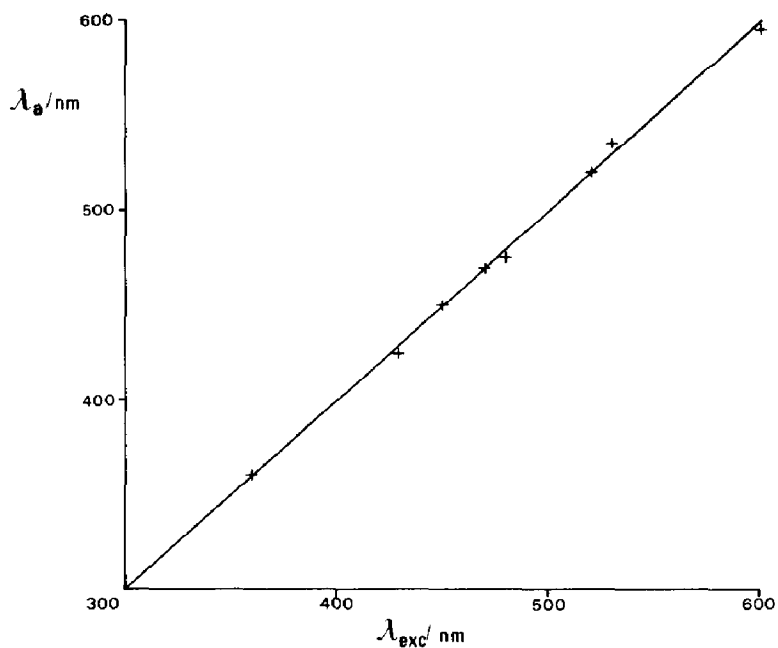

Fig. 4. Correlation between excitation wavelength and maximum decolouration wavelength for a series of monochromatic irradiations of H-cellulose.

simulates the wavelength-intensity features of the excitation beam. This selective action of the irradiation frequencies explains the displacement of the decolouration maximum towards higher wavelengths with increasing thickness encountered in the experiments carried out with $\lambda_{exc} > 290$ nm on a stack of sheets (Fig. 1). Since the diffusion pathway of the photons is a function of their frequency, each sheet can be likened to a filter facing a polychromatic beam of light.

3.3. The reversibility effect: photochromism

For these experiments the cellulose samples were submitted to various cycles of illumination and heating, each specific treatment being followed as a function of time. Figures 5(a) - 5(d) illustrate the case of a sheet of H-cellulose first irradiated at 450 nm (Fig. 5(a)), then heated in the dark at 120 °C (Fig. 5(b)), then re-irradiated at the same λ_{exc} (Fig. 5(c)) and finally re-heated (Fig. 5(d)). The sample taken as the reference for the calculation of the RCN spectrum was that preceding a given treatment. The maxima and minima in the RCN spectra given in Figs. 5(a) - 5(d) coincided *in all instances* with the irradiation wavelength. This behaviour was confirmed with all monochromatic excitations used between 360 and 600 nm.

The reversibility of the colouration-decolouration cycles over the whole range of wavelengths studied demonstrates that the photochromism of cellulose is a general and clear-cut phenomenon.

3.4. The calculation of the decolouration quantum yield

The relative quantum yields $\Phi_{rd\lambda}$ of decolouration were calculated using eqn. (VII) with $k = 1$. Log-log plots of the time dependence of $\Phi_{rd\lambda}$ are shown in Figs. 6 and 7 for simple and double heating-illumination cycles respectively. The relevant observations concerning these results are summarized below.

(i) Φ_{rd} decreases with time. The experimental points for all λ_{exc} used fit straight lines of the general type log $\Phi_{rd} = I + S$ log t.

(ii) The slope of these straight lines is independent of λ_{exc} but increases with the number of heating-illumination cycles.

The values of slope and intercept for the lines shown in Figs. 6 and 7 were calculated by a linear regression procedure and found to be $S' = 0.66 \pm 0.04$ and $I' = 2.26 \pm 0.13$ (one cycle, Fig. 6), and $S'' = 0.81 \pm 0.03$ and $I'' = 1.78 \pm 0.06$ (two cycles, Fig. 7) respectively.

Apart from this systematic study, two experiments were also carried out with laser excitation at 488 nm (argon ion) and 647 nm (krypton ion): the values of the relative decolouration quantum yields and their evolution with irradiation time were close to those reported above.

While it is impossible to propose a detailed rationalization of all the features encountered, some hypotheses can be put forward.

(a) The decrease of Φ_{rd} with reaction time can be interpreted assuming that the decolouration process takes place in two successive photochemical steps and the absorption cross section of the intermediate product is smaller
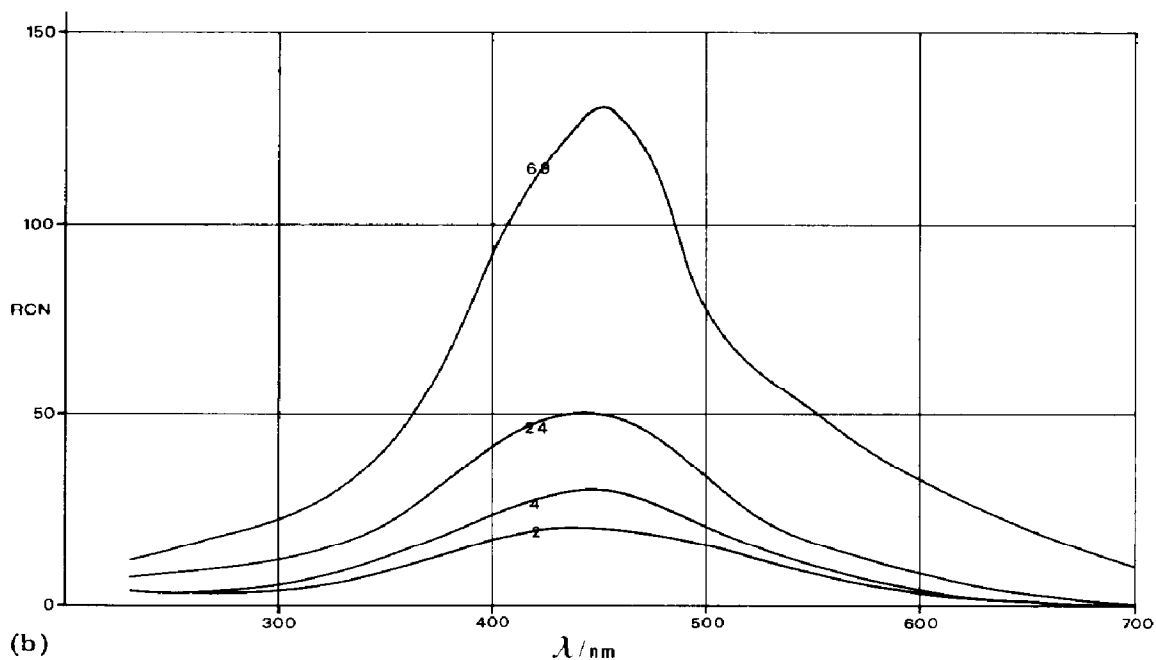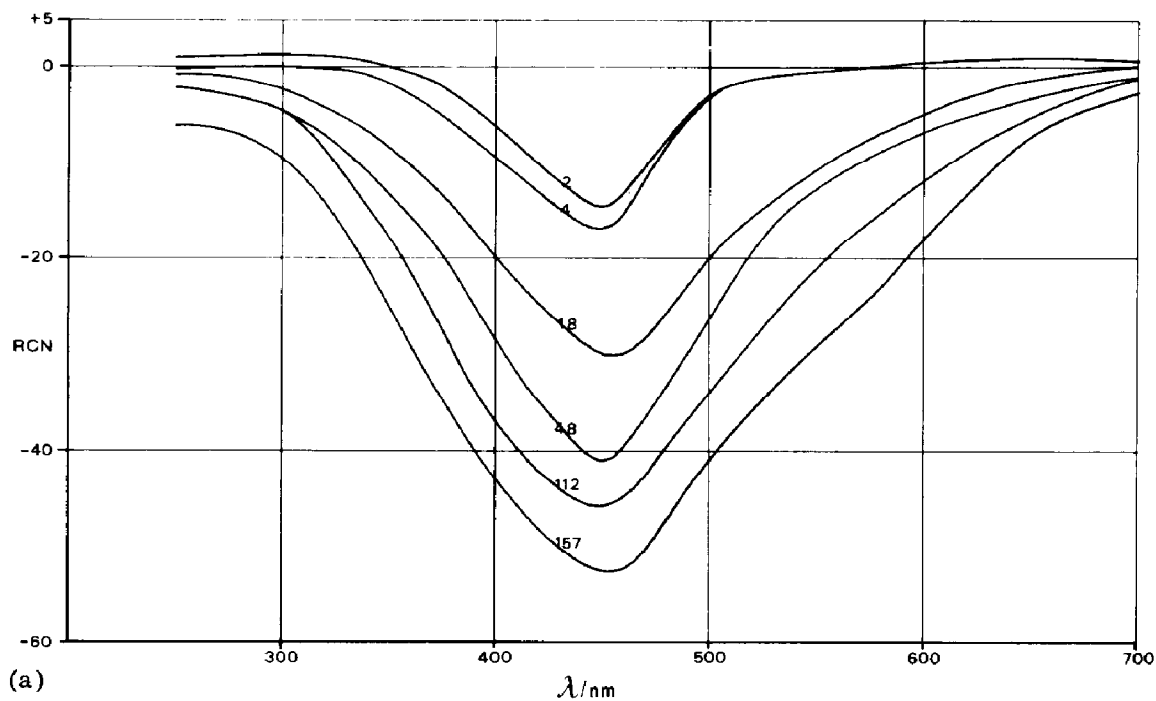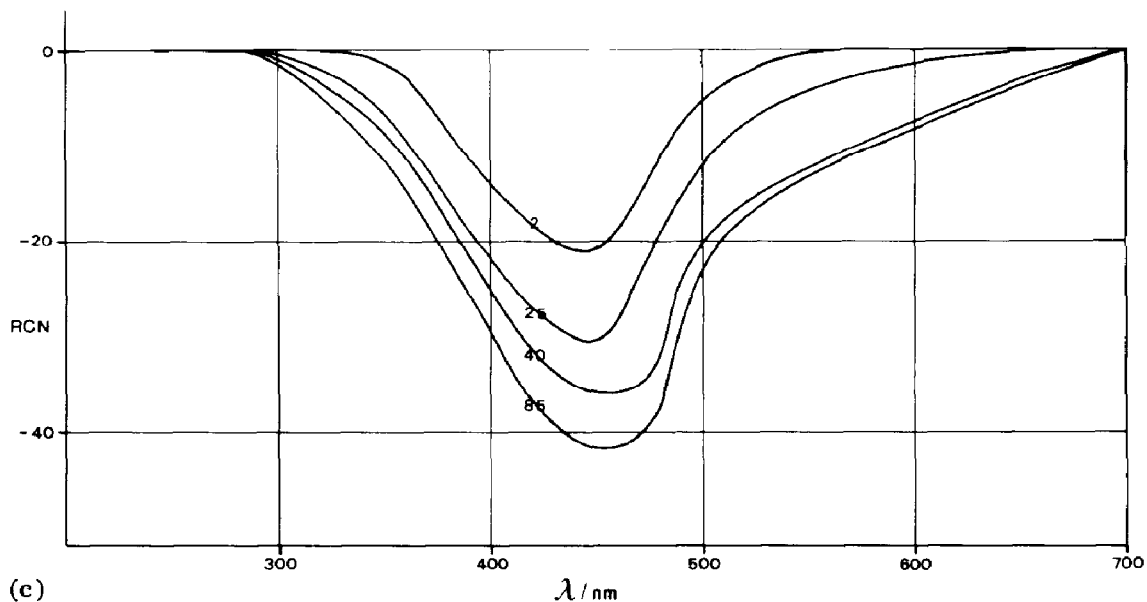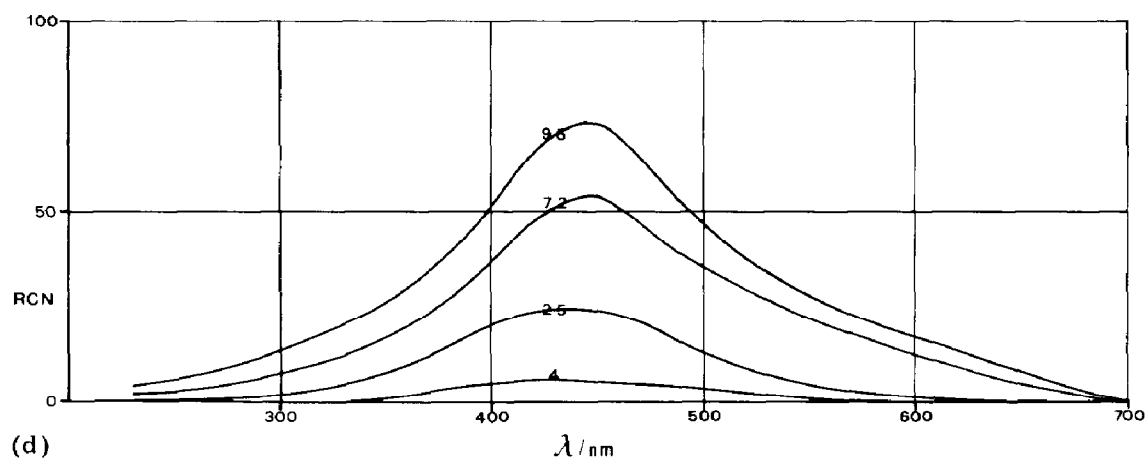
(a)

(b)

Fig. 5 *(continued)*

than- that of the initial chromophores. This would lead to an increasing error in the calculation of Φ_{rd} as the photobleaching proceeds.

  (b) It seems likely that Φ_{rd} is independent of the excitation wavelength. The slight shifts in the straight lines of Figs. 6 and 7 probably arise from

Fig. 5. The reversibility of the decolouration phenomenon with λ_{exc} = 450 nm followed as a function of illumination or heating time (in hours): (a) irradiation of H-cellulose; (b) heating of sample at the end of irradiation (a); (c) irradiation of sample at the end of heat treatment (b); (d) heating of sample after the end of irradiation (c).

systematic experimental errors in the determination of the diffuse reflectance factor (±0.003 optical density units) as well as of the radiant energy reaching the samples. Thus, there is strong (indirect) evidence suggesting that the various chromophores involved in the decolouration process(es) have similar structures, i.e. they belong to a homologous series (for example, a family of polyenes).

The time dependence of the quantum yield of decolouration can be written as
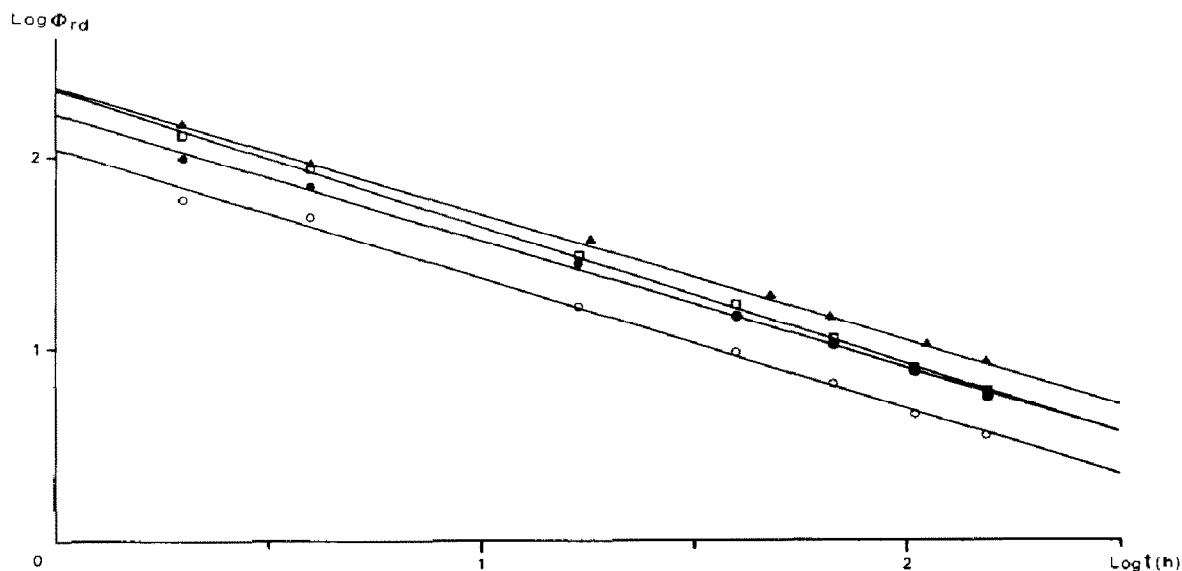
$$\Phi_{rd} = \alpha t^\beta$$

Fig. 6. The variation of the quantum yield of decolouration with irradiation time for a sample of H-cellulose: $\Box$, λ_{exc} = 360 nm; $\bullet$, λ_{exc} = 430 nm; $\blacktriangle$, λ_{exc} = 450 nm; $\bigcirc$, λ_{exc} = 470 nm.
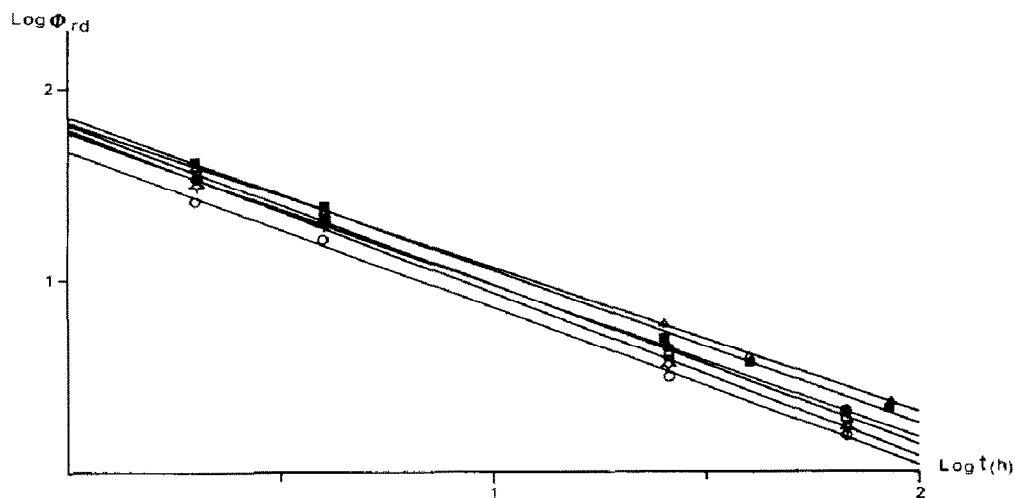

Fig. 7. Same as Fig. 6, but with a sample of H-cellulose which had undergone one illumination and one re-heating treatment. Symbols for λ_{exc} are as in Fig. 6 with: $\triangle$, λ_{exc} = 480 nm; $\star$, λ_{exc} = 520 nm.

where α and β are independent of the excitation wavelength. From Figs. 6 and 7

$$\Phi_{rd} = (182 \pm 56)t^{-0.66 \pm 0.04}$$

for a single heating–illumination cycle, and

$$\Phi_{rd} = (61 \pm 8)t^{-0.81 \pm 0.03}$$

for two complete cycles. The different values of α are due to the different states of the cellulosic substrate, i.e. H-cellulose for the single irradiation and

re-heated bleached cellulose for the second irradiation. Obviously the values of $\Sigma_{a,initial}$ are not the same in the two situations. The small increase in β with the number of cycles could be ascribed to the low incidence of irreversible transformations in the structure of the cellulose, as indeed was noticed in a previous investigation [10].

A thorough understanding of the mechanism of decolouration and colour restoration inevitably requires not only the direct determination of the actual concentration of chromophores, which would allow the calculation of absolute values of $\Phi_{d\lambda}$, but also a knowledge of the chemical nature of these absorbing moieties. Work is in progress towards these goals.

4. Conclusions

The remarkable results obtained for the photochromism of cellulose at wavelengths covering the range 300 - 600 nm and for several cycles of heating and irradiation have amply confirmed previous preliminary findings [10]. The striking additional feature is the faithful coincidence among the excitation wavelength, the absorption minimum in the bleached material and the corresponding absorption maximum which develops upon re-heating the bleached cellulose, a phenomenon which again occurs at all wavelengths studied above 300 nm. The origin of this behaviour is tentatively attributed to the specific destruction and restoration of homologous chromophores.

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