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The UV Spectra of Cellulose and Some Model Compounds

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Synopsis

Comparison of the reflectance spectrum of cellulose with that of myoinositol, cycloheptaamylose, and other model compounds indicates that the acetal linkage does not contribute significantly to the absorption peak at 260 nm. The spectra of photolyzed and photo-oxidized cellulose suggest that ketonic carbonyl groups are a more likely cause of this peak. Photolysis of cellulose and amylose under vacuum with 253.7 nm light increases the concentration of ketonic carbonyls and thus promotes yellowing. Photo-oxidation with 253.7-nm light bleaches both carbohydrates owing to the formation of carboxyl groups. Other investigators had previously reported that this last reaction yellows cellulose, but it appears that this was an effect caused by the 184.9-nm component in the light of the lamp used. Comparison of the spectra of thermally and photolytically yellowed cellulose indicates that the end products of the two degradations are quite different.

INTRODUCTION

Cellulose is photolyzed under vacuum[1] by light of 253.7 nm and, in the presence of oxygen, undergoes a photo-oxidation at 253.7 nm and longer wavelengths.[2-6] Although it has been postulated[7] that carbonyl impurities in the cellulose are the initiators of the photoreaction, that these are not only active centers was illustrated by Flynn et al.[1] who found a poor correlation between the production of CO and CO_2 and the carbonyl and carboxyl content of the cellulose photolyzed. Furthermore, there was a strong indication that the H_2 production was due to the photolysis of hydroxyl groups.

On the basis of the products which were observed from photo-oxidized wood cellulose and related model compounds, Beélik and Hamilton[8,9] postulated the glycosidic linkage to be the initiating center. The absorption spectra of liquid acetals contain a weak absorption peak at ca. 266 nm,[10] and, by analogy, the glycosidic (acetal) linkage in the cellulose was assumed by the above authors to be a weak chromophore, possessing a specific absorption in this region.

A better knowledge of the absorption spectrum of cellulose would help considerably in identifying the nature of the initiating center(s) of the pho-

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tolysis. However, cellulose is fibrous, and hence the large amount of scattered light makes weak absorptions in the transmission spectrum almost impossible to observe. This difficulty has been discussed by Treiber.[11] Attempts have been made to measure the spectrum of solid cellulose directly for example, by dispersing the fibers in a medium of similar refractive index such as LiBr[11] or a suitable oil,[12] by reflectance[13–15] or as films of purified, regenerated cellulose.[5,6] Although conclusive results were not obtained, these investigators agree that the cellulose begins to absorb strongly below about 200 nm, with indications of some absorption between 200 and 300 nm; and a weak absorption peak at ca. 260 nm has been reported.[11,13,15] A weak featureless absorption to about 300 nm would be the spectrum expected from a synthesis of the individual spectra of the functional groups making up the molecule.[16]

We have also studied the 253.7-nm photolysis of cellulose under vacuum[2]; and in order to aid the interpretation of the results, reflectance spectra were taken of cellulose and related compounds, both before and after photolysis. Reflection spectra taken with an integrating sphere have the following advantages: (a) The cellulose does not have to be modified. (b) All the light (both scattered and reflected) can be collected, and hence the ambiguity caused by scattering no longer applies. (c) The observed spectrum can be directly related to the absorption of the cellulose in the photolysis cell.

EXPERIMENTAL

Unmodified Compounds

Reflectance spectra were taken of the series of compounds listed below. Except for myoinositol and glucose itself, the compounds were oligomers and polymers of glucose. All were composed of small crystals and particles with cross sections of less than 0.2 mm and were not sieved. Each sample was dried on a filter paper in an air oven at 105°C for 20 min. This drying was found to have no noticeable effect on the spectra of cellulose and amylose (the only two compounds tested this way), but made the powders very much easier to handle and pack smoothly. They were chosen to determine the effect of the features pointed out below:

(a) A polymer joined by α-1,4 glycosidic linkages: amylose (B.D.H. Biochemical Reagent, from potato starch).

(b) A polymer joined by β-1,4 glycosidic linkages: cellulose (hydrocellulose prepared from cotton cellulose by Meller[17]).

(c) An oligomer, with α-1,4 linkages, but without endgroups: cycloheptaamylose (Koch-Light Laboratories).

(d) A polymer with β-1,3 linkages, and thus containing no vicinal hydroxyls: β-laminarin (Koch-Light Laboratories).

(e) A dimer, containing an equal proportion of endgroups and β-1,4 linkages: cellobiose (B.D.H. Biochemical Reagent).

(f) As for cellobiose, but with α-1,4 linkages: maltose (B.D.H. Laboratory Reagent).

(g) The monomer, containing no linkages: D(+)-glucose (M & B R-Grade).

(h) A compound composed of secondary vicinal hydroxyls only: myo-inositol (Koch-Light Laboratories, Puriss Grade).

Modified Compounds

The hydrocellulose and amylose were treated further to modify the observed spectra.

(a) Some amylose was evacuated at ca. 10^{-6} torr pressure for 24 hr and, without exposure to air at any stage, was transferred to the gas-tight sample cell under dry, oxygen-free nitrogen in a glove box. The spectrum was taken immediately.

(b) A sample of hydrocellulose was heated for 200 hr at 140°C in an air oven.

(c) Samples of amylose were photolyzed with 253.7 nm light from a low-pressure mercury arc (25-watt Oliphant Spiral Lamp, from UV Supplies, Camberwell, Vic.) for 72 hr: (1) under high vacuum (ca. 10^{-6} torr); (2) in dry air. The amylose was spread on the floor of a Vycor cell for the photolysis and, to give a uniform coverage of photolysis products, was stirred frequently by means of a glass-enclosed magnetic stirrer. The light, from the lamp vertically above the cell, passed through 1.0 cm of distilled water to avoid any possible heating effects by IR radiation from the lamp. The sample photolyzed under vacuum was transferred to the reflectance cell as in (a) above.

(d) Samples of hydrocellulose were given identical photolysis treatments as the amylose in (c).

Apparatus

The reflectance spectra were measured in a Beckman DK2A spectrophotometer fitted with an integrating sphere. Both the sphere and the reference sample were coated with Kodak white reflectance paint, freshly applied, which is stated by the manufacturers to have an absolute reflectance over the whole UV range of 96%. The reference plate was covered with a flat silica window. The samples were held in the standard Beckman powder reflectance cell, basically a stainless steel cylinder in which a spring loaded Teflon plunger holds the powders with a slight pressure against a flat silica window, to give a uniformly packed reflecting surface. This powder surface is then in a similar physical condition to that in the photolysis cell used in the photolysis studies of these carbohydrates.[2] A 2-mm layer of powder (assumed to be optically opaque) was used in each case. While the geometry of the sample and reference was adjusted so that the total reflectance (i.e., diffuse + specular) was measured, for ease of comparison with the spectra of reference compounds the instrument was switched

to record apparent absorbance, rather than reflectance. It was found that with the above procedure, the spectra of different samples of the same compound were reproducible to within 0.02 absorbance units.

RESULTS AND DISCUSSION

Unmodified Compounds

The spectra of the unmodified compounds are shown in Figs 1–3. The spectrum observed for glucose agrees with that published by Kortüm.[18] As expected, no strong absorption peaks are observed for any of the compounds, but weak peaks and shoulders are seen in all spectra, with the peak at 260 nm being the most prominent. This absorption is much more distinct than the extremely weak absorption observed in cellulose by Treiber[11] at about this wavelength, and it illustrates the advantages in measuring the reflectance spectrum of the fibrous solid rather than the transmittance spectrum. The peak is very close to the postulated acetal absorption[8,9] at 266 nm and hence should correlate with the acetal linkage content of the compounds studied. It can be seen, however, that the peak, while occurring in the spectra of maltose, amylose, cellobiose, cellulose, and laminarin,

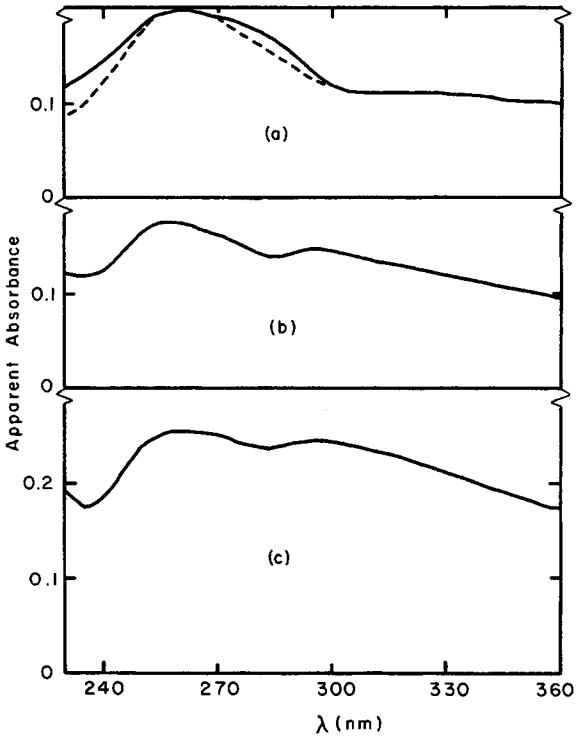

Fig. 1. Reflectance spectra of (a) amylose: (——) in air; (- - -) after evacuation, in nitrogen; (b) hydrocellulose; (c) laminarin.

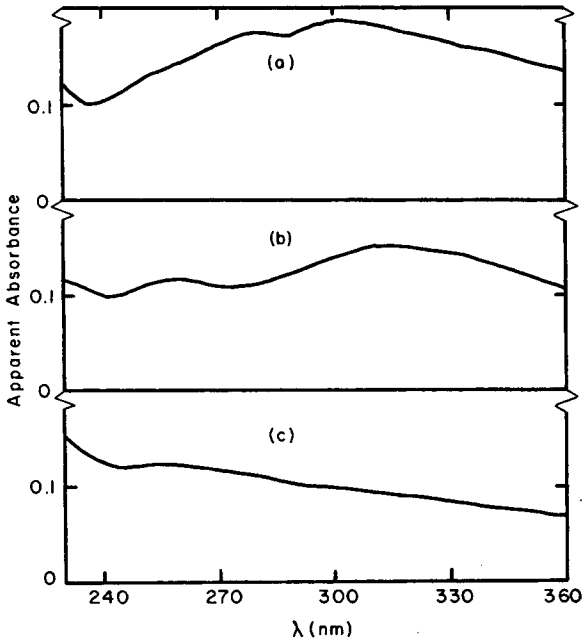

Fig. 2. Reflectance spectra of (a) glucose; (b) myoinositol; (c) cycloheptaamylose.

also occurs in the spectrum of myoinositol, which does not have an acetal linkage. Furthermore, even though cycloheptaamylose has a similar proportion of acetal linkages as the amylose, only a very weak shoulder was observed at 260 nm in the spectrum of the former compound, which suggests that the origin of the 260-nm absortpion peak does not lie in the

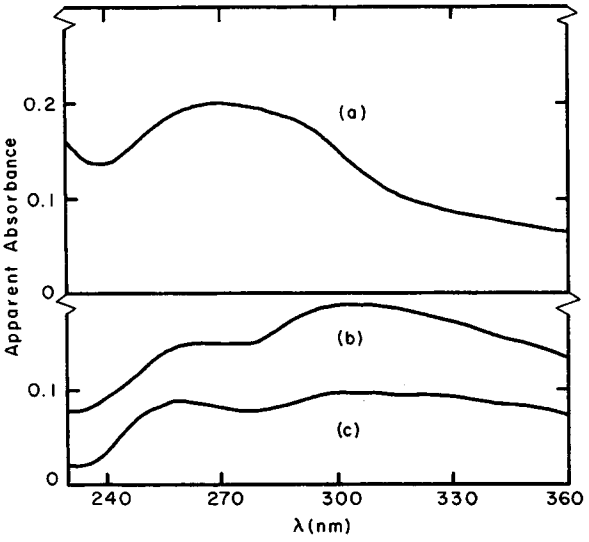

Fig. 3. Reflectance spectra of (a) maltose; (b) cellobiose; (c) freeze-dried cellobiose.

acetal linkage. By similar reasoning, a selective absorption by hydroxyl groups is also ruled out.

The carbohydrate structure can be regarded as composed of alcohol, ether, and hydrocarbon groups joined by aliphatic bonds. The simple members of these groups of compounds are commonly used as solvents for far-ultraviolet spectroscopy and are well known to absorb only weakly to ca. 210 nm.[16] A pure carbohydrate viewed on this basis would therefore be expected to be only weakly absorbing down to this wavelength. The featureless spectrum observed for cycloheptaamylose confirms most closely to this expectation and suggests that it is closest to the true spectrum of a compound with the hypothetical carbohydrate structure. This spectrum shows that if an acetal-linkage selective absorption does exist, it is no stronger than the absorption in this region observed for the other oxygen-containing groups, and hence any selective photolysis or photo-oxidation observed must be attributed to other causes.

Modified Compounds

With the aim of modifying the observed spectrum, and thus elucidating the nature of the species responsible, cellulose and amylose were modified as described in the experimental section.

Stenberg et al.[19] found that ether developed a strong absorption peak at about 210 nm when saturated with oxygen, and this absorption was attributed to an ether–oxygen charge transfer complex. As our spectra were taken in air, this type of complex could be a possible source of the absorption observed at 260 nm. Some effect on the spectrum was observed when amylose was evacuated and the spectrum was taken under nitrogen (Fig. 1a); the peak, although it did not change in intensity, did become sharper, suggesting that only a slight interaction occurs with the oxygen.

Since both the acetal linkage and oxygen complexes appear to be ruled out, a more probable cause of the observed peak at 260 (and 300) nm is therefore an impurity in the carbohydrates. For the carbohydrates, the most likely impurity will be a slight change in the structural units, e.g., a carbonyl or a carboxyl group in place of a hydroxyl group. That it is a very tenacious impurity is shown by the spectrum of cellobiose recrystallized and freeze-dried from conductivity water (Fig. 3c). Although the overall light absorption is less (partly caused by the smaller particle size[18]), both the 260- and the 300-nm peaks are still apparent, indicating that if impurities are the cause of these peaks, they will substitute quite closely into the host lattice. The structural differences must therefore be minor.

As to the nature of the impurity, in Figures 4 and 5 are shown the spectra of amylose and cellulose after photolysis and photo-oxidation, and, for comparison, of cellulose after heating in air. The physical appearance under low magnification (40×) of the powders given these treatments was not different from the original compounds, but the heated hydrocellulose

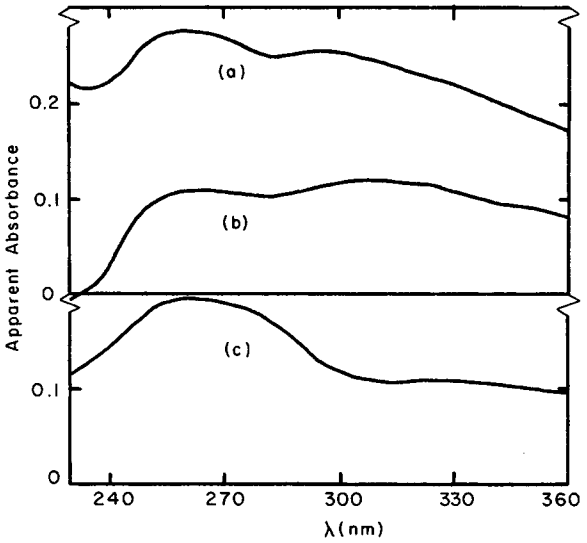

Fig. 4. Reflectance spectra of modified amylose: (a) photolyzed in vacuum; (b) photolyzed in dry air; (c) original.

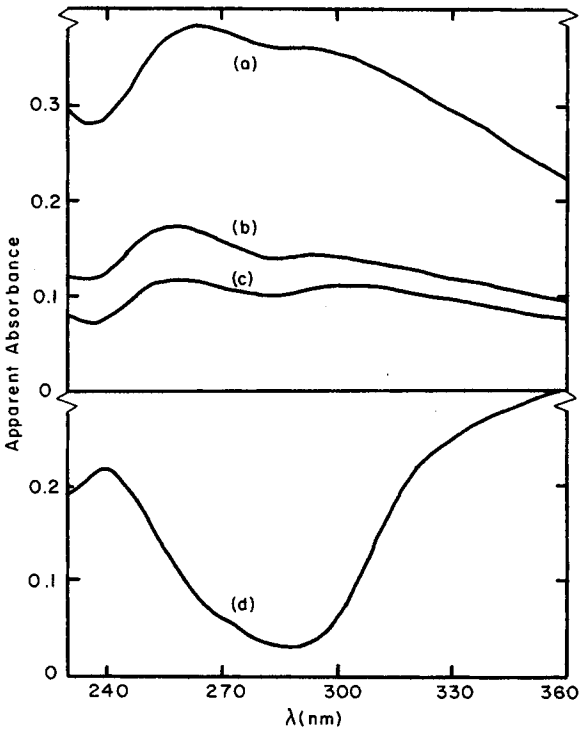

Fig. 5. Reflectance spectra of modified hydrocellulose: (a) photolyzed in vacuum; (b) original; (c) photolyzed in dry air; (d) thermally oxidized at 140°C.

was very yellow, and the two vacuum-photolyzed compounds were slightly so.

In the case of cellulose, no new peaks form on photolysis, but the spectrum changes intensity as a whole, the peaks at 260 and 300 nm increasing or decreasing together according to the atmosphere. The spectrum observed for amylose changes on photolysis to one very similar to that of cellulose, with the intensity also increasing on photolysis under vacuum and decreasing on photolysis in air. In other words, when the cellulose and amylose were photolyzed in dry air they were bleached, while if they were photolyzed under vacuum they became more colored, i.e., they became yellowed.

These results are in sharp contrast to those reported by Launer and Wilson.[3] These authors photolyzed wood and cotton cellulose with the light from a low-pressure mercury lamp and found that the celluloses yellowed in all cases, whether the atmosphere was O_2 or N_2. The reason for this different behavior appears to lie in the difference in the spectrum of the light incident upon the cellulose. In our case, the 184.9-nm line of the low-pressure mercury arc was filtered out by the Vycor cell window. As the major proportion of the light output from the lamp is in the resonance line at 253.7 nm, and since the quantum yield for cellulose photolysis at longer wavelengths is very small,[2,5] it appears that in our experiments we observed photolysis and photo-oxidation by 253.7-nm light only. In the experiments of Launer and Wilson, the sheet of paper was wrapped around the lamp. This type of lamp had a quartz envelope,[20] which transmits the 184.9-nm line. Although the ratio of the intensities of the 184.9-nm to the 253.7-nm line is of the order of 1:17,[21] we have found that the inclusion of the former in the photolysis can increase the rate of H_2 evolution (and hence carbonyl formation[1]) from cellulose under vacuum by a factor of eight.[2] Kujirai has found that, while the 253.7-nm photolysis of cellulose is dependent on the oxygen pressure, and has postulated the formation of carboxyl groups in the photo-oxidation at this wavelength, the 184.9-nm photolysis appears to be independent of oxygen; and from the appearance of an intense absorption at 260 nm he has postulated the formation of aldehyde groups during this photolysis. The lack of dependence on the surrounding atmosphere for the yellowing of cellulose as found by Launer and Wilson supports the possibility that their photolysis was a combined one by 184.9 nm and 253.7 nm. At wavelengths longer than 253.7 nm, i.e., 330 to 750 nm, cellulose also bleaches.[3]

Our reflectance spectra show that the same products are formed in amylose on photolysis under vacuum as are formed in cellulose. The absorption peaks of these products are at the same wavelengths as the original peaks in the unphotolyzed cellulose. It would appear, therefore, that the original absorption spectrum of the carbohydrates is due to a small quantity of compounds similar to those formed during the photolysis.

The absorbing groups in photolyzed cellulose are limited to those containing C, H, and O. Of the possibilities, only conjugated olefins and carbonyl

groups have absorption peaks at wavelengths greater than 250 nm, so that the two observed peaks must be due to some combination of these two functional groups. If olefinic double bonds are formed, they will be adjacent to a hydroxyl group because no water is produced on photolysis under vacuum.[2] We have photolyzed hydrocellulose for 170 hr under vacuum with 253.7-nm light and tested the product with $FeCl_3$ solution. No color reaction was observed, indicating that no enols were present.[2] Furthermore, the infrared spectrum of regenerated cellulose photolyzed under vacuum for a similar length of time showed no absorption peak at 1620 cm^{-1}, the frequency expected for double bonds, although an absorption peak did occur at 1720 cm^{-1}, the carbonyl stretching frequency.[2] Similarly, Beélik and Hamilton[8] found that no reductones, such as the ascorbic acid suggested by Laurent and Wertheim,[22] were formed in photo-oxidized cellulose. This means that the two peaks at 260 and 300 nm must be solely due to carbonyl species, unsaturated carbonyl species being excluded by the absence of any infrared absorption peak which could be attributed to double bonds. In water, dihydroxyacetone absorbs at 268 nm, acetone at 265 nm, and acetaldehyde at 289 nm. The 1,2-dicarbonyl of cyclohexane absorbs at 380 and 298 nm. Our spectra were not taken past 360 nm so that it is not possible to distinguish the 300 nm peak as an aldehyde or a 1,2-diketone from the spectrum. However, as Flynn et al.[1] have found that aldehydes were formed on photolysis of cellulose under vacuum with 253.7 nm light, part of the 300-nm absorption peak will probably be due to aldehyde groups. Furthermore, from the published λ_{max} of aldehydes and ketones, the peak at 260 nm appears to be due to a ketonic carbonyl rather than the aldehyde suggested by Kujirai.[5]

Although cellulose reacts more when photolyzed in oxygen than in nitrogen,[2,6] the peaks at 260 and 300 nm decrease on photo-oxidation, and the spectra show that the products formed on photolysis in air do not absorb ultraviolet light above 240 nm. The only groups possible in cellulose with this characteristic are hydroxyls, ethers, and carboxyls. A possibility remains that carbonyl groups formed on photolysis and photo-oxidation were hydrated to the *gem*-diol by contact with moist air in the transfer to the reflectance cell, but since photo-oxidized celluloses were shown to contain carboxyl groups but no ketonic nor aldehydic carbonyls,[6,8] the reason for the bleaching of the cellulose and the amylose on photolysis in dry air seems to be the oxidation of carbonyls to acids. Very little concentration of hydroperoxy and peroxy groups is built up, judging from the lack of absorption at 240 nm, where these groups begin to have appreciable extinction coefficients.

Comparison with Thermal Oxidation

While aldehyde and carboxyl groups have also been found on thermal oxidation of cellulose[23] at 150°C, the spectrum in Figure 5d shows that the actual composition of these groups in thermally decomposed cellulose is different to the groups in photolyzed cellulose. If it is assumed that the

long-wavelength peak in Figure 5d is due to carbonyl groups, its marked red shift from the absorption maximum of simple carbonyls indicates considerable conjugation. As water is the main product of low-temperature thermal oxidation of cellulose,[24] considerable crosslinking and double-bond formation is possible by the elimination of H_2O from neighboring OH groups, intra- or intermolecularly. The basic reactions occurring in thermal and photolytic decompositions are therefore quite different, and this is clearly reflected in the spectra.

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References

1. J. H. Flynn and W. L. Morrow, *J. Polym. Sci. A*, **2**, 81, 91 (1964).
2. A. Bos, Ph.D. Thesis, University of Melbourne, 1970.
3. H. F. Launer and W. K. Wilson, *J. Amer. Chem. Soc.*, **71**, 958 (1949).
4. G. S. Egerton, E. Attle, F. Guirguis, and M. A. Rathor, *J. Soc. Dyers Colour.*, **79**, 49 (1963).
5. C. Kujirai, *Sen-i-Gakkaishi*, **21**, 183 (1965); *C. A.* **63**, 8598f.
6. C. Kujirai, *Sen-i-Gakkaishi*, **21**, 260 (1965); *C. A.*, **64**, 3823e.
7. O. B. Zapol'skii, *Polym. Sci. USSR*, **3**, 114 (1962).
8. A. Beélik and J. K. Hamilton, *Das Papier*, **13**, 77 (1959).
9. A. Beélik and J. K. Hamilton, *J. Org. Chem.*, **26**, 5074 (1961).
10. J. Schurz and E. Kienzl, *Monatsh. Chem.*, **88**, 78 (1957).
11. E. Treiber, *Kolloid-Z.*, **130**, 39 (1953).
12. J. D. Dean, C. M. Fleming, and R. T. O'Connor, *Text. Res. J.*, **22**, 609 (1952).
13. G. Champetier and R. Marton, *Bull. Soc. Chim. France, Ser. 5*, **10**, 102 (1943).
14. R. J. Brysson and B. J. Trask, *Text. Res. J.*, **36**, 753 (1966).
15. G. O. Phillips, *Ric. Sci. Quad.*, **66**, (1970).
16. DMS *U.V. Atlas of Organic Compounds*, Butterworths, London, 1967.
17. A. Meller, *Svensk Papperstidn.*, **65**, 307 (1962).
18. G. Kortüm, *Reflectance Spectroscopy*, Springer-Verlag, New York, 1969, p 148.
19. V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967).
20. General Electric, Overseas Lamp Dept., personal communication.
21. J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, **56**, 37 (1960).
22. T. C. Laurent and E. M. Wertheim, *Acta Chem. Scand.*, **6**, 678 (1952).
23. R. C. Waller, K. C. Bass, and W. E. Roseveare, *Ind. Eng. Chem.*, **40**, 138 (1948).
24. W. D. Major, *Tappi*, **41**, 530 (1958).

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