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A Study of the Fluorescence of Cellulosic Polymers

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INTRODUCTION

Many polymeric materials fluoresce when activated by suitable ultraviolet radiation. While there are numerous reports in the literature relating to the fluorescence of fibers,[1-3] rubber,[4-6] cellulose,[7-11] polymers,[12-20] and plastics,[21-23] these are frequently based on subjective observations of fluorescence and on the use of broad spectrum sources of ultraviolet as activating energy. Instrumental measurements of fluorescence were generally made with polymer solutions, and in many cases fluorescence was reported as a side effect or interfering phenomenon. Fluorescence has been used to study polymerization and also to follow the progress of vulcanization of rubber.

The development of instrumentation to control the wavelength of the activating energy and to measure the resulting fluorescence emission spectra now provides a means of describing more accurately the fluorescence of materials. Jortner[24] measured the fluorescence of cellulose and cellulose acetate with a fluorescence attachment on a spectrophotometer.

This report describes the use of a commercial spectrophotofluorometer[25] to study the fluorescence of a series of cellulosic polymers.

EXPERIMENTAL

Materials

The cellulose derivatives studies are listed in Table I. They include an uncoated cellophane and a series of cellulosic polymers selected to provide a broad spectrum of materials. There are ten cellulose esters with aliphatic side groups of several chain lengths and of several different degrees of substitution. A fairly wide range of molecular weights is covered, as indicated by the viscosities. The other polymers were selected to provide a variety of side groups. All data concerning degree of substitution of the various side groups as well as the viscosities are those provided by the manufacturers.

Films were cast on glass plates from appropriate solvent solutions. The films were removed and dried in air for a minimum of one month prior to examination with the spectrophotofluorometer. No plasticizer or other additive material was used. The uncoated cellophane included in the study was extracted for 6 hr. with 95% ethanol and then air-dried for about 72 hr. before it was studied.

Equipment and Methods

The fluorescence measurements were made with a spectrophotofluorometer illustrated schematically in Figure 1. Selected portions of the radiation from a xenon arc lamp were directed on the specimen by a grating monochromator. The fluorescence emitted by the specimen was dispersed by a similar monochromator to a photomultiplier tube (1P21). The photomultiplier tube signal was amplified and fed to the y-axis of a cathode-ray oscillograph or to an x-y recorder. The x-axis was controlled by the wavelength setting of the monochromator.

The instrument was designed for use with solutions but in this study was adapted for use with solid materials such as plastics, films, cloth, paper, and fibers by means of a specially designed specimen holder. This device held the specimen at any angle from 0° to 180° to the exciting light beam. In this investigation the samples were mounted at an angle of approximately 95° to the excitation light beam, and the fluorescence was measured from the edge and back surface of the specimen. Variation in specimen thickness caused considerable variation in the total measurable fluorescence but did not affect the shape of the spectral curve. The effect of film thickness is illustrated in Figure 2, which shows the fluorescence intensity of a series of carboxymethyl cellulose films of various thicknesses. It is apparent that film thickness has a marked effect on fluorescence. Other factors that

TABLE I
Film-Forming Cellulose Polymers

Film number	Material	Manufacturer
0	Cellophane, uncoated, Type 600 P-2	Sylvania
1	Cellulose acetate, Type WH-2, acetyl 58.5%, visc. 165 sec.	Hercules
2	Cellulose acetate, Type E-27, acetyl 39.6–40.4%, visc. 1–4 sec.	Eastman
3	Cellulose acetate, Type A 393-55, acetyl 39.4%, visc. 62 sec.	Eastman
4	Cellulose acetate, Type E 400-25, acetyl 40.1%, visc. 23 sec.	Eastman
5	Cellulose propionate, propionyl 44.9%, visc. 80-110 sec.	Celanese
6	Cellulose acetate propionate, Type AP-141-95, acetyl 30.0%, propionyl 14.0%	Eastman
7	Cellulose acetate butyrate, Type EAB-381, acetyl 6%, butyryl 27.1%, visc. 0.5 sec.	Eastman
8	Cellulose acetate butyrate, Type EAB-171-15, acetyl ca. 30%, butyryl ca. 18%	Eastman
9	Cellulose acetate butyrate, Type EAB 500-5, acetyl 6.5%, butyryl 48.0%	Eastman
10	Cellulose trideconate	Eastman
11	Ethyl cellulose, No. L-355, ethoxy 48.8%, visc. 22 sec.	Dow
12	Methyl cellulose, medium viscosity	Dow
13	Cellulose nitrate, visc. 22 sec.	Hercules
14	Benzyl cellulose, high viscosity	Hercules
15	Carboxymethyl cellulose, medium viscosity	Hercules
16	Cellulose acetate sorbate, medium viscosity	Hercules
17	Cellulose acetate hydrogen phthalate, acetyl 17–22%, phthalyl 30–40%	Eastman

may cause variations in fluorescence intensity are surface roughness of the specimen, flatness of the film in the holder, the absorption characteristics of the film with respect to the exciting and emitted radiations, and instrumental variables.

Since the instrument is intended for use with solutions, considerable difficulty is encountered with scattering when working with solid specimens. In this study scattering was not a problem when radiation with a wavelength less than 280 mμ was used to excite the fluorescence. Between 280 and 310 mμ a Raman scatter appears, and at longer wavelengths a Rayleigh-type scatter is obtained. The Raman-type scatter produces scatter peaks in the fluorescence spectrum at about 20 mμ higher than the wavelength of the exciting light. The Rayleigh-type scatter appears at the same wavelength as that of the exciting radiation. Scatter of these types are identified and described more

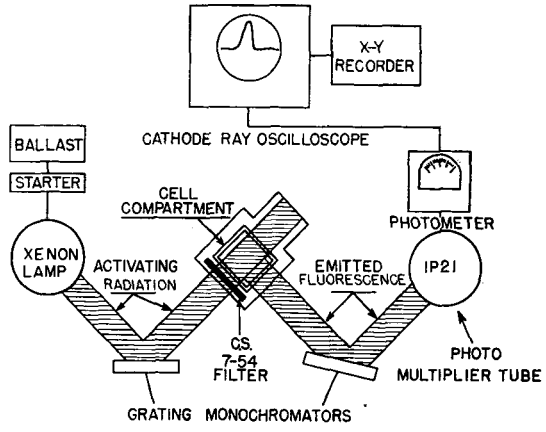

Fig. 1. Schematic drawing of the spectrophotofluorometer.

completely by Price[26] and Parker.[27] These scatter effects are particularly troublesome when a material fluoresces at wavelengths close to the wavelength of the exciting radiation. The excitation beam of the instrument is not pure monochromatic radiation but contains some long wavelength radiation. As a result, two strong, narrow peaks located at about 465 and 570 mμ are found in the fluorescence spectra of some cellulosic films. These peaks are eliminated by the insertion of an untraviolet-transmitting, visible-absorbing filter of red-purple

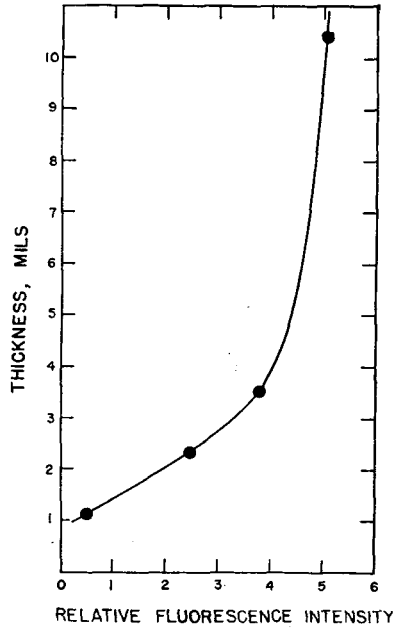

Fig. 2. Relative fluorescence intensity of a series of carboxymethyl cellulose films (Film 15).

Corning glass No. 9863, C. S. No. 7-54, in the exciting radiation path at the point where the radiation enters in the specimen compartment.

The instrument was calibrated with quinine sulfate according to the method of Sprince and Rawley.[28]

Ultraviolet absorption curves were obtained for all films with a spectrophotometer. All curves were similar to those reported in the literature for similar polymers and for that reason are not included here.

RESULTS AND DISCUSSION

Most of the fluorescent curves were obtained at an exciting wavelength of 290 mμ. In a few instances when 290 mμ excitation produced a small scatter peak at about 310 mμ an exciting wavelength of 285 mμ was used.

The cellulosic polymers consistently fall into three groups based on the wavelength of the fluorescence maximum, the relative intensity of the fluorescence, and the chemical structure of the material. Three typical fluorescence curves are shown in Figure 3. Curve (*1*) is a typical cellulose nitrate fluorescence curve. The fluorescence is weak and attains its maximum at 320 mμ. In this figure the cellulose nitrate curve has been amplified tenfold in order to facilitate comparison with the other curves. The intensity of the fluorescence of cellulose nitrate in the region of 320 mμ, when compared with the fluorescence intensity of other cellulosic compounds, was probably weakened by absorption of either the exciting radiation or of the

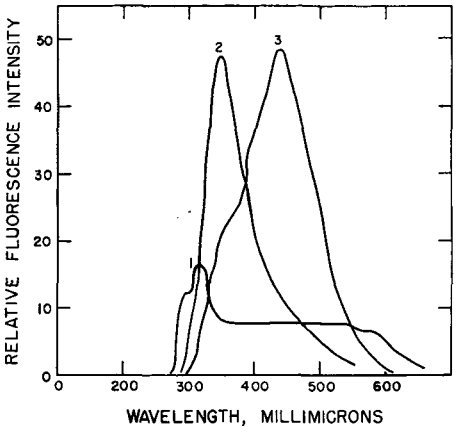

Fig. 3. Fluorescence spectra of cellulosic films: (*1*) cellulose nitrate (Film 13); relative fluorescence intensity magnified tenfold; (*2*) cellulose esters; (typical of Films 1–10) scale × 1; (*3*) cellulosic polymers containing complex side groups (typical of Films 14–17), relative fluorescence intensity magnified threefold.

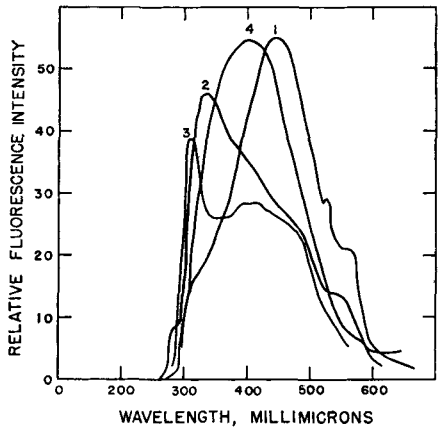

Fig. 4. Fluorescence spectra of cellophane and cellophane reaction products: (*1*) cellophane (Film 0); (*2*) acetylated cellophane; (*3*) nitrated cellophane; relative fluorescence intensity magnified tenfold; (*4*) sodium borohydride-treated cellophane.

emitted light, by the nitro groups. Curve (*2*) is typical of aliphatic esters of cellulose, with a fluorescence maximum at about 350 mμ. Aliphatic side groups with as many as ten carbon atoms had no influence on the position of the maximum. Molecular weight also had no effect. Cellulose ethers yield similar fluorescence curves; the maxima for methyl and ethyl cellulose occurring at 360 and 340 mμ, respectively. Curve (*3*), with a fluorescence maximum at about 440 mμ, is typical of cellulose derivatives containing either double bonds or carboxyl groups. Those with double bonds include benzyl cellulose, cellulose acetate hydrogen phthalate, and cellulose acetate sorbate. The carboxyl-containing polymers include carboxymethyl cellulose and cellophane. The intensity of this curve was amplified threefold.

A number of experiments were carried out to test the apparent relationship between chemical structure and fluorescence. The results of the first set of experiments are illustrated in Figure 4. Curve (*1*) is a typical cellophane curve featuring a broad peak at about 440–450 mμ. Specimens of the cellophane were immersed in acetic anhydride for various periods of time. The specimens were removed, washed thoroughly with distilled water, and dried overnight. The fluorescence maximum was found to shift with time of acetylation until, after 4 hr., curve (*2*), with a sharp peak at 340 mμ, was obtained. The wavelength range of this maximum was about the same as that of the cellulose esters but the intensity was much less. A cellophane specimen was nitrated with a HNO_3–H_2SO_4–H_2O (4:2:1) mixture for 2 hr.; this yielded

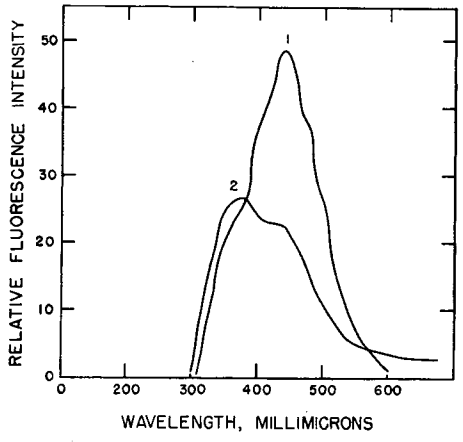

Fig. 5. Fluorescence spectra of benzyl cellulose films: (*1*) benzyl cellulose (Film 14), (*2*) sodium borohydride-treated benzyl cellulose.

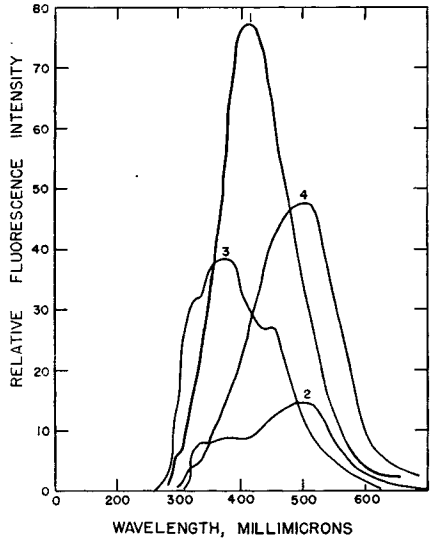

Fig. 6. Fluorescence spectra of cellulose acetate sorbate films: (*1*) cellulose acetate sorbate (Film 16); (*2*) brominated cellulose acetate sorbate, (*3*) oxidized cellulose acetate sorbate; (*4*) heat-treated cellulose acetate sorbate.

curve (*3*), which is similar to the curve for the cellulose nitrate film with a peak at 310 mμ at an exciting wavelength of 285 mμ. Again, the ordinate of this curve is enlarged ten times in order to facilitate comparison with the other fluorescence curves. Curve (*4*) was obtained with a cellophane specimen that had been treated with sodium borohydride solution to react with such reducing groups as carbonyls and hemiacetals. The treatment caused the fluorescent peak to shift from 440–450 mμ to about 400 mμ. This is the direction of shift that might be expected if the proposed relationship between fluorescence and structure is correct. Other work in this laboratory has shown that purified cotton cellulose consistently fluoresces at about 365 mμ.

Another experiment to test the relationship of structure and fluorescence was carried out with benzyl cellulose film. The fluorescence spectrum of this film, curve (*1*), Figure 5, features a sharp peak with a maximum at 440 mμ. Benzyl cellulose treated with sodium borohydride to remove the benzyl groups produced curve (*2*). The curve has a peak at 370 mμ, very close to the 365 mμ fluorescence peak of cellulose. The curve retains a shoulder at 440 mμ, indicating the possible presence of some remaining benzyl groups.

Another series of experiments was performed with cellulose acetate sorbate which contains a six carbon side group having a pair of conjugated double bonds. A typical cellulose acetate sorbate fluorescence curve, shown in curve (*1*) of Figure 6, features a peak at about 430 mμ. Bromination of this film produced the results shown in curve (2). In this case the fluorescence was very much reduced and the main peak shifted to about 480–500 mμ. This change may be attributed to the heavy bromine atoms in the compound. Another experiment consisted of oxidizing the film with 30% hydrogen peroxide at room temperature for various periods of time. As the time of oxidation increased the peak shifted toward the shorter wavelengths. After 8 hr. curve (*3*) was obtained with 285 mμ excitation; here, the main peak was at 370 mμ, while a trace of the original peak remained as a small shoulder on the curve. This shift is attributed to the replacement of the double bonds with hydroxyl groups to yield a polysaccharidelike structure. Curve (*4*) was obtained from a cellulose acetate sorbate after heat treatment. The film was heated at 150°C. for a total of 3 hr. and fluorescence spectra were obtained at 1-, 2-, and 3-hr. intervals. The fluorescent peak moved from 420 to 490 mμ in 1 hr. It moved to 500 mμ during the second hour of heating, after which no further change occurred. The film became pale yellow during the first hour, and the color intensity appeared to increase during the additional heating periods. Apparently the degradation that occurred caused the shift to longer wavelengths.

Several attempts were made to hydrogenate the double bonds in cellulose acetate sorbate. These attempts were unsuccessful, since the methods used for hydrogenation plus the procedure necessary to separate the product from the catalyst reduced the degree of polymerization to

such an extent that it was impossible to prepare a film of the polymer.

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Synopsis

A spectrophotofluorometer, suitably modified for use with plastics films, was used to study a series of cellulosic polymer films. The chemical structure of the films was found to be related to the wavelength and intensity of the fluorescence emission spectra. Saturated aliphatic esters and ethers were found to possess strong fluorescence maxima at about 350 mμ. Cellulose nitrate exhibits very weak fluorescence at 310 mμ, and a moderate fluorescence maximum appears at 440 mμ for cellulose derivatives containing double bonds or carboxyl groups. A series of experiments is described in which the modification of chemical structure was followed by measuring changes in fluorescence spectra.

Résumé

Pour étudier une série de films de polymère cellulosique on a utilisé un spectrophotofluoromètre spécialement modifié pour l'étude de films plastiques. On a trouvé que la structure chimique des films est en relation avec la longueur d'onde et avec l'intensité du spectre d'émission de fluorescence. On a trouvé que les esters et les éthers aliphatiques saturés possédaient de fort maxima de fluorescence à environ 350 mμ. Le nitrate de cellulose présente une très faible fluorescence à 310 mμ, et un maximum modéré de fluorescence apparait à 440 mμ pour les dérivés de la cellulose contenant des doubles liaisons ou des groupes carboxyliques. On décrit une série d'expériences dans lesquelles la modification de structure chimique a été suivie par la mesure de variations dans le spectre de fluorescence.

Zusammenfassung

Ein zur Untersuchung von plastischen Filmen entsprechend abgeändertes Spektrophotofluorometer wurde zur Untersuchung einer Reihe von Cellulosepolymerfilmen verwendet. Es wurde gefunden, dass die chemische Struktur in Beziehung zur Wellenlänge und Intensität der Fluoreszenzemissionsspektren steht. Gesättigte aliphatische Ester und Äther besitzen scharfe Fluoreszenzmaxima bei ungefähr 350 mμ. Cellulosenitrat zeigt eine sehr schwache Fluoreszenz bei 310 mμ; Cellulosederivate, die Doppelbindungen oder Carboxylgruppen enthalten, zeigen ein mässiges Fluoreszenzmaximum bei 440 mμ. Es wird eine Reihe von Versuchen beschrieben, bei denen die Änderung der chemischen Struktur durch Messung der Änderungen der Fluoreszenzspektren verfolgt wurde.

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