

Photosensitive Polymers. I. Cinnamate Esters of Poly(vinyl Alcohol) and Cellulose*

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INTRODUCTION

After Niepce¹ discovered the inherent but low light-sensitivity of Syrian asphalt in 1815, few references to other nonaqueous, light-sensitive coatings appeared until 1926. In that year Beebe, Murray, and Herlinger² disclosed that iodine compounds such as iodoform or colloidal lead iodide photosensitize coatings of partly gelled drying oils, such as tung oil. Exposures of such coatings to ultraviolet radiation and to blue light caused them to become insoluble in prior solvents. Differential solubilities also were obtained after exposure to ultraviolet radiation with various natural and synthetic resins by including in the coatings such light-sensitive α,β -unsaturated compounds as dicinnamalacetone.³

Low order of sensitivity and limited differential solubility were characteristic of the above-mentioned systems. However, the coatings remained chemically stable for many years, in contrast to the short-term stability in storage of better-known, water-sensitive dichromate- or diazo-sensitized natural gum and protein colloid coatings.

The classical photochemical study of cinnamic acid by Stobbe and co-workers,⁴ begun in 1919, is well known. In 1934, Malm and Fordyce⁵ disclosed that sheets of unsaturated esters of cellulose, such as cellulose tricrotonate, may be insolubilized by 5 hours' exposure to intense ultraviolet radiation or by heating at 100°C. for 24 hr.^{2b} In 1947, Allen and VanAllan⁶ found that cinnamoylated polystyrene exhibited ultraviolet-sensitivity. Their material, however, suffered from low sensitivity and low differential solubility.

The present paper⁷ describes a study of the light-sensitivity of cinnamic acid esters of cellulose and poly(vinyl alcohol), with some attention to the effect of degree of reaction, molecular weight as

indicated by viscosity, and substitution on the cinnamoyl group. Whereas early poly(vinyl cinnamate) coatings showed no significant gain in sensitivity over earlier polymers, they showed infinite differential solubility between exposed and unexposed polymer in a wide range of solvents, and high stability before exposure. In the initial photosensitivity tests, the cinnamate polymers were coated from solvents on glass plates in subdued room light. The dried coatings were placed in contact with a coarse half-tone photographic transparency in a glass-covered exposing frame, and were exposed to the radiation from a 35-amp. Macbeth White Flame carbon arc. When the exposed plates were bathed in the coating solvent, the unexposed areas of polymer coating dissolved, while the exposed areas of polymer were insoluble and remained on the plate to form an uncolored image which was difficult to discern.

It is the usual practice in the graphic arts to add a dye like Crystal Violet carbinol (usually 5-10%) to improve the visibility of a developed image. Comparison of exposure tests of coatings containing Crystal Violet carbinol with those not containing the dye indicated that Crystal Violet carbinol had definitely increased the response of the polymers to the exposing radiation. Moreover, it produced varying levels of sensitivity with differently substituted cinnamate polymers.

SENSITOMETRY

To provide a semiquantitative measure of the response of a polymer to light and to ultraviolet radiation, therefore, an exposure test was devised based on the following principles of photographic sensitometry: The photosensitivity value S of a polymer coating can be defined as the reciprocal of the exposure E required to insolubilize the polymer in a prior coating solvent under a standard set of conditions. Thus, where k is a constant,

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$$S = k/E \quad (1)$$

Since the exposure E is the product of the illuminance I of the exposing light source in meter-candles and the exposure time t in seconds, then

$$S = k/It \quad (\text{meter-candle-sec.}^{-1}) \quad (2)$$

Rather than determining the sensitivity of a coating by finding either the exposure time or the intensity of the light source that renders the coating insoluble, it is more convenient to interpose a neutral-density light filter between the source and the coating under test. The transmittance T of the filter is the ratio between transmitted illuminance and incident illuminance on the filter. The photographic density D of the filter is the logarithm of the reciprocal of transmittance and is readily measured on a densitometer. Thus, in expanded form, the equation for the sensitivity value becomes

$$S = k/ITt = (k \text{ antilog } D)/It \quad (3)$$

In practice, a photographic step tablet is placed in contact with the polymer coating during exposure. In this way a series of different exposures is produced in a coating in a single exposing operation. Narrow strips of many coating samples can be given a series of exposures simultaneously.

By use of a photometer, the illuminance in meter-candles of an exposing source can be calibrated accurately. By exposure of a coating to the calibrated source for a measured time through a step tablet with calibrated densities, the sensitivity value of the coating can be calculated from eq. (3).

In order to minimize the effects of coating thickness and of variables other than photosensitivity, the following testing procedure was adopted as standard.

One volume of 10% solution of the polymer in chlorobenzene (1 g. to 10 ml. solvent) was diluted with three volumes of toluene, in which all addenda had been dissolved. This solution was then coated by whirling on a paper lithographic printing plate and dried at 50°C. A strip of this coating under glass in a vacuum printing-frame was exposed through a 0.15-density step tablet to the light source at such a distance that one minute at least was required to give a satisfactory image. The image was developed by rocking in a tray for 2 min. with methyl ethyl ketone, rinsed by rocking for 1 min. with fresh methyl ethyl ketone, and dried at 50°C. The strips were swabbed with methanol, treated with preservative (obtained from Addressograph Multigraph Corp., Cleveland, Ohio), dried, and

hand-inked with a black, oily ink. Ink is accepted by those areas covered by polymer and rejected elsewhere. The exposure time for the step midway between complete acceptance and complete rejection was used to calculate the photosensitivity value in eq. (3). Unless otherwise specified, the light source was a 35-amp. Macbeth White Flame carbon arc providing continuous emission in the visible and ultraviolet regions of the spectrum.

By this method, the sensitivity value of undyed, unsensitized poly(vinyl cinnamate) was determined as 2.2×10^{-8} meter-candle-sec.⁻¹. To simplify placement of the decimal point, the constant k in the sensitivity value equation was taken to be 10^8 . Thus, the value for the sensitivity of unsensitized poly(vinyl cinnamate) is represented as 2.2.

Experimental evidence has shown that the sensitivity of unsensitized poly(vinyl cinnamate) coated from the standard chlorobenzene-toluene mixture is remarkably constant at 2.2. Moreover, it obeys the reciprocity law; that is, the sensitivity value is the same for a short-duration, high-intensity exposure as for a long-duration, low-intensity exposure. An unsensitized poly(vinyl cinnamate) of known history was adopted as a control to avoid having to monitor the exposing conditions continually with a photometer. A control strip was exposed simultaneously with each series of sample coatings. The sensitivity values of the sample coatings were calculated in terms of the control sensitivity value, by use of the following equation:

$$\begin{aligned} S_x &= S_c \frac{\text{antilog } D_x}{\text{antilog } D_c} \\ &= \text{antilog} (\log 2.2 + D_x - D_c) \\ &= \text{antilog} (0.33 + D_x - D_c) \end{aligned} \quad (4)$$

where subscripts X and c refer to the sample and the control strip, respectively.

EXPERIMENTAL AND RESULTS

Although a number of poly(vinyl and cellulose cinnamates) were prepared, only the procedure used for the preparation of poly(vinyl cinnamate) is given in detail here, since the others were prepared identically or with only minor modifications of this method.

The poly(vinyl alcohols) used were commercial samples, designated as low-, medium-, and high-viscosity poly(vinyl alcohols). The respective inherent viscosities of different lots of these were about 0.3, 0.8, and 1.0 in water at a concentration

of 0.25 g./100 ml. of solution. Cinnamic acid esters were also prepared from regenerated cellulose, cellulose monoacetate, and hydroxyethyl cellulose.

Preparation of Poly(vinyl Cinnamates)

Eleven grams of poly(vinyl alcohol) were suspended in 100 ml. of pyridine (Eastman Grade) in an all-glass reflux apparatus protected from moisture by a calcium chloride tube and heated overnight on a steam-bath. One hundred ml. of pyridine was added and, after the reaction mixture had been cooled to 50°C., 50 g. of cinnamoyl chloride (Eastman Practical Grade), warmed sufficiently to melt, was poured in, in portions, with shaking. At this stage, the addition product of pyridine and cinnamoyl chloride precipitated. The reaction flask was then immersed in a 50°C.-bath for 4 hr., with occasional stirring, during which time a viscous dope and a crystalline precipitate formed. The viscous dope was diluted with 4 volumes of

acetone, filtered through glass cloth by suction, and poured into distilled water, with stirring, to precipitate the polymer. The fibrous product was washed with distilled water until it was free from chloride ion and dried in darkness in a vacuum desiccator over calcium chloride under a constantly applied water-pump vacuum. Samples were analyzed for carbon, hydrogen, and distinctive groups present. When no distinctive group was present, the amount of reaction was calculated from the carbon and hydrogen values.

Effect of Degree of Esterification on the Photo-Response of Poly(vinyl Cinnamate)

In order to determine the effect on sensitivity of incomplete reaction during the preparation of the poly(vinyl cinnamates), a series of poly(vinyl alcohols) with a range of substitution by cinnamoyl were prepared. To obtain a narrow distribution of cinnamoyl content in any one given sample, the series were prepared by back-hydrolysis of a sample which had been essentially completely esterified. The back-hydrolysis was carried out in pyridine solution by the addition of 40% aqueous trimethyl benzyl ammonium hydroxide. The reaction was left at room temperature until alkalinity to phenolphthalein disappeared. No phase separation occurred. The solution was then diluted with acetone, poured into water, and vigorously stirred to precipitate the product. The latter was washed thoroughly with water and dried at 40°C. The response to light of each sample was determined by the standard procedure when solubility permitted; the insoluble samples, as indicated in Table III, were coated from and developed by pyridine.

TABLE I
Poly(vinyl Cinnamates)

Poly(vinyl alcohol)	Substitution on phenyl	Combined vinyl cinnamate, wt.-%	Unsensitized sensitivity value
Low	—	94	0.15
Medium	—	97	2.2
High	—	95	2.2
Medium	<i>o</i> -Chloro	96	2.2
Medium	<i>m</i> -Nitro	88	350
Medium	α -Phenyl	90	0.15
Medium	β -Phenyl	79	0.15

TABLE II
Cellulose Cinnamates

Parent polymer	Substitution on phenyl	Combined triester, wt.-%	Unsensitized sensitivity value
Cellulose	—	94	9
Cellulose monoacetate	—	55	1.1
Cellulose monoacetate	<i>o</i> -Chloro	51	1.1
Cellulose dihydroxyethyl ether	—	—	4.5
Cellulose dihydroxyethyl ether	<i>m</i> -Nitro	63	650

TABLE III
Effect of Cinnamoyl Content upon the Sensitivity of Cinnamoylated Poly(vinyl Alcohol)

Combined vinyl cinnamate, mole-%	Testing procedure	Sensitivity value
100.0	Standard	2.2
90.5	Standard	2.2
87.0	Standard	2.9 ^a
81.5	Standard	3.1 ^a
100.0	Pyridine	6.1 ^b
76.0	Pyridine	6.1
71.0	Pyridine	6.1
66.5	Pyridine	6.1

^a This increase in sensitivity-value may not be significant, owing to loss of solubility.

^b Pyridine acts, to a degree, as a sensitizer.

Effect of Sensitizers Added to Polymer Solutions

In addition to the sensitizing action exhibited by Crystal Violet carbinol, it was observed that the test solutions of polymers containing the sensitizer increased in sensitivity value with aging. The effects of concentration and aging are shown in Table IV.

TABLE IV
Effect of Crystal Violet Carbinol (CVB) Concentration and Dope Age on Sensitivity

CVB concn., % ^a	Sensitivity value after aging of dope				
	Fresh	2 Days	3 Weeks	6 Weeks	8 Weeks
Control	2.2	2.2	2.2	2.2	2.2
0.1	5.2	7.0	3.8	—	—
0.25	7.0	7.0	7.8	—	—
0.5	7.5	9.8	6.5	—	—
1.0	9.2	14	13	12	—
2.5	22	22	40	44	—
5.0	29	29	150	150	220
10	38	38	250	—	—
25	43	43	250	310	310

^a Based on dry weight of polymer.

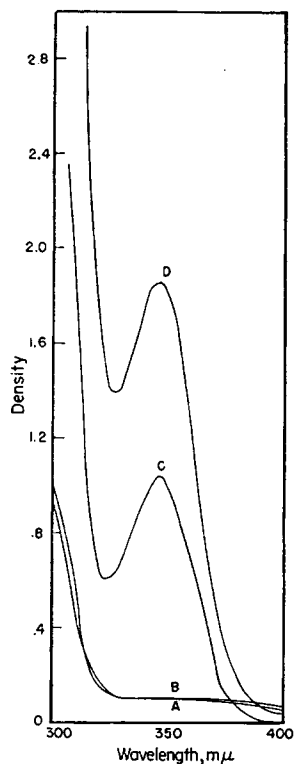


Fig. 1. Ultraviolet absorption by poly(vinyl cinnamate) dopes: (A) fresh, unsensitized; (B) fresh, Crystal Violet carbinol added; (C) fresh, Michler's ketone added, $1/125,000$ dilution; (D) ten months old, containing Crystal Violet carbinol $1/25,000$ dilution.

Crystal Violet carbinol is known to decompose to yield Michler's ketone. A coating dope of poly(vinyl cinnamate) in chlorobenzene-toluene was prepared by the standard test procedure. Portions of this dope were sensitized by 10% Michler's ketone and by 10% Crystal Violet carbinol. The significant regions of the ultraviolet absorption curves of these portions and of a standard dope aged for 10 months with 10% Crystal Violet indicate conclusively the presence of Michler's ketone in the aged dope (see Fig. 1). However, the complete absence of any peak in the unaged carbinol-containing dope indicates, too, that the carbinol is a sensitizer in its own right. The sensitizing behavior of Michler's ketone is given in Table V.

TABLE V

Sensitizing Behavior of Michler's Ketone	
Concn., % ^a	Sensitivity value
0	2.2
2	280
4	450
8	550
10	650
14	650
20	650
50	650

^a Based on dry weight of polymer.

A Crystal Violet carbinol-sensitized dope, aged for 86 weeks, for which the ultraviolet absorption curve showed the formation of 3.3% of Michler's

TABLE VI
Effect of Peroxides on Sensitivity of Poly(vinyl Cinnamate) Coatings

Peroxide concn., %	Unsensitized sensitivity value	
	Fresh	Aged 2 weeks
Control	2	2
Benzoyl peroxide		
1	2	5
3.3	2	50
10	2	Gel
<i>tert</i> -Butylperbenzoate		
1	2	7
3.3	2	7
10	2	7
<i>Di-tert</i> -butyldiphephthalate		
1	2	5
3.3	2	5
10	2	5
Cyclohexanone peroxide		
1	2	2
3.3	2	2
10	2	2

TABLE VII
Spectral Sensitivities of Sensitized Poly(vinyl Cinnamate)^a

Sensitizing compound	Sensitivity value	Strength of absorption lines				
		435.8 m μ	407.8, 404.7 m μ	366.3, 365.5, 365.0 m μ	334.2 m μ	313.2, 269.8 m μ
Control (unsensitized)	2	—	—	+	2+	3+
Crystal Violet dye	40	+	2+	3+	2+	3+
<i>p</i> -Nitrosodimethylaniline	1	+	+	2+	2+	3+
Diethylthiacarbobenzothiazole	2	—	—	+	2+	3+
Diethylthiacarbocyanine <i>p</i> -toluenesulfonate	2	—	—	+	2+	3+
Diethylmethylthiacarbocyanine bromide	3	—	—	+	2+	3+
Acetanilidovinylbenzothiazole ethiodide	10	2+	2+	3+	2+	3+
<i>p</i> -Nitrodimethylaniline	60	3+	2+	3+	2+	3+
<i>p</i> -Nitroaniline	100	2+	2+	3+	2+	3+
Auramine O Base	90	3+	2+	3+	2+	3+
Diethylbenzothiacyanine chloride	200	3+	2+	+	+	3+

^a — = absent; + = weak; 2+ = medium; 3+ = strong.

ketone, had a sensitivity value of 300. This compares favorably with that of a fresh dope sensitized directly by an equal amount of the ketone.

Because peroxides are known to sensitize ultraviolet-catalyzed polymerization of double bonds, their behavior in this system was examined. As shown in Table VI, peroxides do not act as sensitizers in the fresh cinnamate system. With aging, there is a small increase in sensitivity value with ultimate gelation of the dope. This would indicate a low-level crosslinking during aging, which would manifest itself as an increase in response as long as the polymer remained soluble.

The spectral sensitivities of unsensitized and 10% sensitized poly(vinyl cinnamate) coatings are given in Table VII. These coatings were made according to the standard procedure and were exposed on a Hilger spectrograph to a 250-watt U-Viarc mercury vapor lamp for 24 hr through a sectored wheel. Standard development and inking were used. Examination of the spectral lines indicates a definite increase in response in the longer wavelengths with increase in sensitivity value.

In a subsequent paper, the behavior of a large number of organic compounds in a medium-viscosity poly(vinyl cinnamate) system will be discussed.

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Synopsis

Cinnamic acid esters of poly(vinyl alcohol) and of cellulose are insolubilized by ultraviolet radiation. This response may be increased by the inclusion of simple organic compounds such as Crystal Violet carbinol and Michler's ketone. A method of measuring this response (in terms of a sensitivity value, *S*) based upon photographic sensitometry has been devised. Preliminary study indicates that an increase in *S* is accompanied by an increase in response to the longer wavelengths of light.

Résumé

Les esters cinnamiques de l'alcool polyvinylique et de la cellulose sont insolubilisés par irradiation ultraviolette. Cet effet peut être accru par inclusion de composés organiques simples tels le carbinol du violet cristallisé et la cétone de Michler. Une méthode de mesure de cet effet (valeur sensibilisatrice *S*) basée sur la sensitométrie photographique a été mise au point. Une étude préliminaire indique qu'une

augmentation de S est accompagnée d'une augmentation de la réponse à l'égard de plus grande longueur d'ondes lumineuses.

Zusammenfassung

Zimtsäureester von Polyvinylalkohol und von Cellulose werden durch Ultraviolettbestrahlung unlöslich. Diese Wirkung kann durch Einschluss einfacher organischer Ver-

bindungen wie des Carbinols von Kristallviolett und Michlers Keton vergrößert werden. Eine Methode zur Messung dieses Effektes (des Empfindlichkeitswertes S), die auf photographischer Sensitometrie beruht, wurde angegeben. Eine vorläufige Untersuchung zeigt, dass bei einer Zunahme von S gleichzeitig eine Zunahme der Wirkung des längerwelligen Lichts erfolgt.

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