

## Photosensitive Polymers. II. Sensitization of Poly(vinyl Cinnamate)\*

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### INTRODUCTION

In Part I,<sup>1</sup> the photoinsolubilization of cinnamic esters of cellulose and poly(vinyl alcohol) was described, and the early work on the increase of this response by the inclusion of simple organic compounds was summarized. This paper continues with the investigation of the sensitization of medium-viscosity poly(vinyl cinnamate). Various compounds, including hydrocarbons, amines, nitro compounds, ketones, aldehydes, quinones, anthrones, thiazoles, etc., were tested by the standard procedure under glass absorbing below 3500 Å. Spectral sensitivities of coatings containing a large number of these are included.

### EXPERIMENTAL AND RESULTS

The sensitometry involved in determining the response to light of the various polymer-sensitizer combinations is similar to that given earlier.<sup>1</sup> In order to increase reproducibility of the test by compensating for variations beyond control, a control coating of unsensitized poly(vinyl cinnamate) of sensitivity value 2.2 was included in each exposure group. The entire apparatus was placed in a ventilated enclosure and a light-integrating device was installed which improved the reproducibility over that obtained by timing the exposure. In those cases where the addend lacked solubility in the standard solvent combination, a maximum of 10% methyl alcohol was added. If dissolution was still incomplete, the mixture was filtered. Errors introduced in these instances were few since, for most sensitizers, 10% methanol provided adequate solubility for the 5 to 10% optimum sensitizer concentration range.

Spectrograms were made of many of the coatings, with a Bausch and Lomb Monochromator which had been adapted for use as a spectrograph. It was equipped with quartz optics and a grating.

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The light source was an 800-watt, high-pressure xenon lamp and a 0.3 density-gradient Inconel-on-quartz step wedge was used at the entrance slit of the instrument. A typical exposure with a 1.0-mm. slit was 5 min. In Table I are given the sensitization results, peak sensitivity, and extension of sensitivity (when available) of a number of compounds selected to illustrate types and trends,<sup>2</sup> and Figure 1 shows some typical spectrograms. Table II shows the effect of the arrangement of reducing groups in additives upon the sensitivity of poly(vinyl cinnamate), and Table III demonstrates the effect on sensitizing action of compounds that contain neighboring groups that interact, probably through hydrogen-bridging.

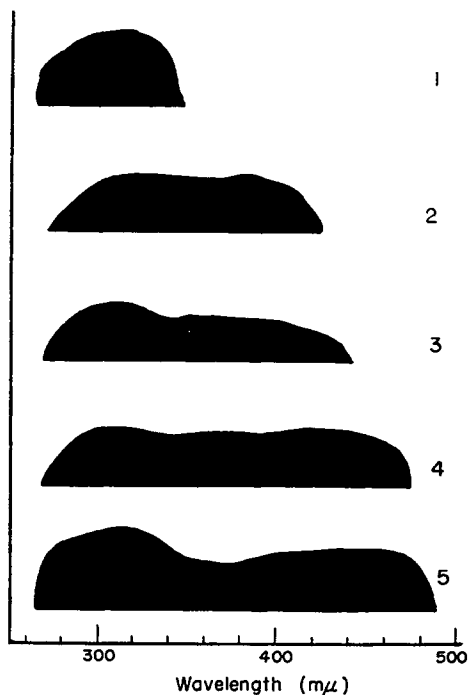


Fig. 1. Typical spectrograms of sensitized poly(vinyl cinnamate). (1) Unsensitized, (2) *p*-nitroaniline, (3) 2,4-dinitroaniline, (4) picramide, and (5) 3-methyl-1,3-diaza-1,9-benzanthrone.

TABLE I  
Sensitizing Activity of Compounds and Spectral Sensitivity of Coatings

No.	Sensitizing compound	Sensitivity value	Sensitizer peak sensitivity, $m\mu$	Furtherest extension of sensitivity, $m\mu$
0	None	2.2	320	340
Hydrocarbons				
1	Naphthalene	2.6		
2	Anthracene	7.7		
3	Phenanthrene	14		
4	Chrysene	18		
Amino, Nitro, Phenolic Compounds				
5	Nitrobenzene	7.9		
6	<i>p</i> -Dinitrobenzene	37		
7	1,3,5-Trinitrobenzene	12		
8	<i>p</i> -Nitrodiphenyl	180	360	380
9	<i>m</i> -Nitroaniline	51		
10	<i>p</i> -Nitroaniline	110	370	400
11	2,4-Dinitroaniline	88	360	440
12	Picramide	400	450	480
13	2-Chloro-4-nitro-nitro aniline	290	380	410
14	2,6-Dichloro-4-nitro aniline	330	380	410
15	Phenol	1.8		
16	<i>p</i> -Nitrophenol	70		
17	2,4-Dinitrophenol	7.9		
18	2,4,6-Trinitrophenol	17		
Ketones				
19	Benzaldehyde	6.8		
20	9-Anthraldehyde	35		
21	Acetophenone	2.6		
22	Benzophenone	20		
23	Dibenzalacetone	60		
24	Benzil	46		
25	<i>p,p'</i> -Diaminobenzophenone	35		
26	<i>p,p'</i> -Dimethylaminobenzophenone	510		
27	<i>p,p'</i> -Tetramethyldiaminobenzophenone	640	380	420
Quinones				
28	Benzoquinone	2.2		
29	1,2-Naphthoquinone	21		
30	1,4-Naphthoquinone	57		
31	Anthraquinone	99	320	420
32	1,2-Benzanthraquinone	510	420	470

TABLE I (continued)

No.	Sensitizing compound	Sensitivity value	Sensitizer peak sensitivity, $m\mu$	Furtherest extension of sensitivity, $m\mu$
Anthrones				
33	Anthrone	31		
34	1,9-Benzanthrone	90	320	330
35	6-Phenyl-1,9-benzanthrone	11		
36	3-Phenyl-1,9-benzanthrone	1.6		
37	2-Keto-3-aza-1,9-benzanthrone	55		
38	3-Methyl-1,3-diaza-1,9-benzanthrone	1100	470	490

TABLE II  
Inhibition of Sensitivity by Reducing Groups

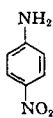

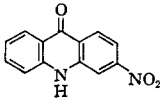
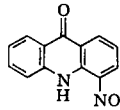
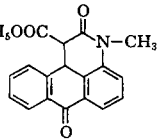
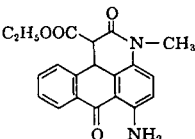
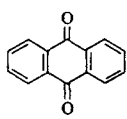
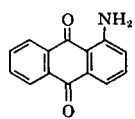
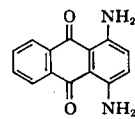
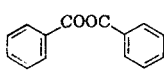
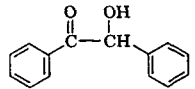
Compound	Sensitivity value
Hydroquinone	1.8
<i>o</i> -Aminophenol	2.1
<i>p</i> -Aminophenol	1.5
<i>o</i> -Phenylenediamine	1.6
<i>p</i> -Phenylenediamine	— <sup>a</sup>
Nitrosodimethylaniline	1.0
Dicinnamalazine	— <sup>a</sup>

<sup>a</sup> No detectable sensitivity within limits of the test.

## DISCUSSION

It is quite apparent that poly(vinyl cinnamate) is sensitized to ultraviolet radiation and visible light by a large variety of compounds. It appears that the ability to sensitize is general among all compounds tested except those which are rendered inactive through reductive effects as in hydroquinone, hydrazines, *o*- and *p*-aminophenols, nitroso compounds, or through hydrogen-bridging or "adjacency" effects as in *o*-nitrobenzaldehyde, 2-aminonaphthoquinone, and others listed in Table III. The enhancement in activity due to the introduction into a nucleus of added conjugation, of nitro, keto, amino groups, or combinations of these is evident, provided no complications mentioned earlier are introduced. For a given poly(vinyl cinnamate) coated and developed under a standard set of conditions, an increase in sensitivity value is accompanied by an increase in absorption with a shift toward the visible spectrum, but it does not follow that compounds having absorption in those regions will be sensitizers.

TABLE III  
 Depression of Sensitization by Adjacency Effects

Sensitizer	Sensitivity value	Sensitizer	Sensitivity value
	110		1.5
	110		<sup>a</sup>
	510		<sup>a</sup>
	99		5.1
			<sup>a</sup>
	46		7.7

<sup>a</sup> No detectable sensitivity within the limits of the tests.

Two mechanisms suggest themselves to explain the sensitizing action of organic compounds upon poly(vinyl cinnamate). The first involves true photosensitization, in which the addend is activated by the light and, in turn, activates the double bonds of the cinnamoyl group to undergo either a vinyl addition or a truxillic type of dimerization, most probably the latter. The second mechanism involves the activation of the double bond by the light to undergo the vinyl addition or truxillic dimerization. The addend, activated by the light, acts like a transfer agent in vinyl polymerizations to transfer energy from a reacted and isolated cinnamoyl group to another cinnamoyl group too far away to react normally. The latter now starts a new crosslink. In either case, the observed result will be earlier insolubilization of the poly(vinyl cinnamate), due to an increase in the number of crosslinkages per unit of light or time of exposure. It should be pointed out that there are many similarities between the behavior of poly(vinyl

cinnamate) and rubber under the same conditions.<sup>3</sup> The behavior of rubber, however, is complicated by a response to oxygen which poly(vinyl, cinnamate) does not appear to show.

## References

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- L. M. Minsk, W. P. Van Deusen, and E. M. Robertson (assigned to Eastman Kodak Co.), U.S. Patent 2,610,120 (1952); U.S. Patent 2,670,285 (1954); U.S. Patent 2,670,286 (1954); U.S. Patent 2,670,287 (1954).
- (a) R. Pummer and H. Keblen, *Ber.*, **66**, 1107 (1933); (b) I. Ostromislensky, *J. Russ. Phys. Chem. Soc.*, **44**, 204 (1912); (c) Davis and Blake, *Chemistry and Technology of Rubber*, Am. Chem. Soc. Monograph, Reinhold, New York, 1937, Chap. 7.

## Synopsis

It was reported in Part I of this series that coatings of various polymers containing cinnamic ester groups are rendered insoluble by exposure to ultraviolet radiation, and that the rate of insolubilization may be increased by the inclusion of certain organic compounds. A continued systematic examination of the behavior of several hundred organic compounds has revealed that the ability to sensitize to some degree is quite general, provided that no complicating factors are present. The sensitivity of poly(vinyl cinnamate) is decreased by the presence of reducing groups in the addend, and sensitizing activity is lowered by interaction between adjacent groups. It is enhanced by the introduction of increasing conjugation and of ketone, nitro, or amino groups. Spectrograms of polymer-sensitizer combinations indicate that, with increasing sensitivity value, the sensitivity shifts towards, and, in some cases, into, the visible portion of the spectrum.

## Résumé

Dans le premier article on a décrit l'insolubilité progressive de revêtement de divers polymères contenant des esters cinnamiques sous l'influence de l'irradiation ultraviolette; la vitesse d'insolubilisation peut être accrue par l'inclusion de certains dérivés organiques. Un examen poursuivi systématiquement de nombreuses substances organiques révèle que la sensibilisation à un certain degré est général, pourvu qu'il n'y a pas de facteurs compliquants le système. La sensibilité du cinnamate de polyvinyle est décrie par la présence de groupes réducteurs au sein de l'additif; son activité sensibilisatrice est diminuée par interaction avec des groupes adjacents. Par contre, elle est favorisée par la présence d'une conjugaison plus forte et par des groupes cétoniques, nitrés ou aminés. Les spectrogrammes des combinaisons polymère-sensibilisateur indiquent que, avec une valeur croissante de la sensibilité, celle-ci glisse vers et parfois même atteint la partie visible au spectre.

## Zusammenfassung

In der ersten Mitteilung dieser Reihe wurde berichtet, dass Überzüge aus verschiedenen Polymeren, die Zimtsäureestergruppen enthalten, durch Einwirkung von ultra-

violetter Strahlung unlöslich gemacht werden und dass die Geschwindigkeit dieses Vorganges durch Einschluss gewisser organischer Verbindungen erhöht werden kann. Die fortgesetzte systematische Überprüfung des Verhaltens einiger hundert organischer Verbindungen hat ergeben, dass die Fähigkeit zu einer gewissen Sensibilisierung eine sehr allgemeine ist, vorausgesetzt, dass keine komplizierenden Faktoren vorhanden sind. Die Empfindlichkeit von Polyvinylcinnamat wird durch die Gegenwart von reduzierenden Gruppen im Zusatz vermindert und die Sensibilisierungs-

wirkung wird durch die Wechselwirkung zwischen benachbarten Gruppen herabgesetzt. Sie wird durch Einführung einer stärkeren Konjugation und von Keto-, Nitro- oder Aminogruppen verstärkt. Spektrogramme von Polymer-Sensibilisatormischungen lassen erkennen, dass bei Zunahme des Empfindlichkeitswertes, die Empfindlichkeit sich gegen und, in einigen Fällen, in den sichtbaren Teil des Spektrums verschiebt.

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