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Some Experiments on the Triplet State Mechanism of the Spectral Sensitization of Poly(vinyl cinnamate) and Its Application for Searching New Sensitizers*[1]

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The spectral sensitization of poly(vinyl cinnamate) is considered to occur by the triplet energy transfer from sensitizer to the cinnamoyl group of the polymer. The triplet state mechanism is useful for finding new sensitizers. Some new sensitizer were found on the basis of the theory, and the results may verify the mechanism.

Ultraviolet light irradiation on poly(vinyl cinnamate) reduces the solubility of the polymer according to the dose of light. The main response of cinnamic acid and its esters to photons is believed to be their dimerizations. The dimerization of cinnamoyl groups attached to polymers results in crosslinking of the polymer, which produces the insolubilization of the polymer.

The photosensitivity of poly(vinyl cinnamate) is limited to wavelengths shorter than 340 mμ, but the addition of some organic compounds confers sensitivity on the portion of the spectrum absorbed by those compounds;[1,2] hence, these compounds are spectral sensitizers. The experimental fact that the better sensitizers are aromatic nitro compounds and aromatic cabronyl compounds, suggests that the energy transfer may occur from the triplet state (T-state) of sensitizers to that of the cinnamoyl group (Fig. 1). The proposed mechanism clearly explained the experimental results on the sensitivities of mixed sensitizers which have different lowest triplet levels.[3] In the present paper we will report a search for new sensitizers based on the T-state mechanism; this will be a test for the mechanism.

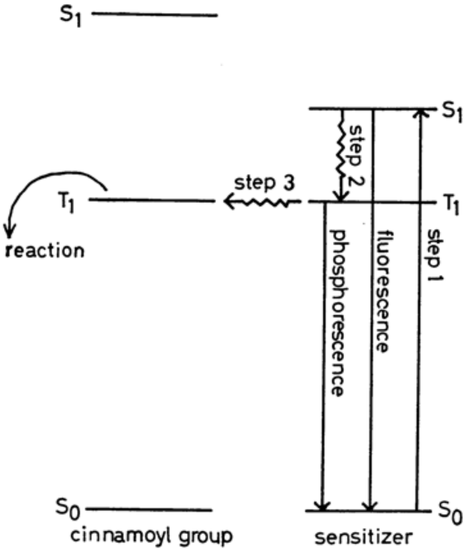


Fig. 1. Energy transfer diagram in spectral sensitization of poly(vinyl cinnamate).

Experimental

Poly(vinyl cinnamate) was prepared by the method reported in previous papers.[4] The polymer was purified by precipitation in methanol.

2,6-Dichloro- and 2,6-Dibromo-*N,N*-dimethyl-4-nitroaniline. Br$_2$(3.7 g) or Cl$_2$(0.92 g) was added into a methanol (200 m*l*) solution of *N,N*-dimethyl-4-nitroaniline (1.7 g), and the solution was refluxed for 2.5 hr. A large portion of methanol was distilled off, and crystals formed on standing. Recrystallized from ethanol.

Br-Derivative: mp 113.5—114.5°C. Found: C, 29.55; H, 2.40; N, 8.79; Br, 50.88%. Calcd for $C_8H_8N_2O_2Br_2$: C, 29.66; H, 2.49; N, 8.65; Br, 49.33%.

Cl-Derivative: mp 106—107°C. Found: C, 40.72; H, 3.71; N, 11.54; Cl, 29.71%. Calcd for $C_8H_8N_2O_2Cl_2$: C, 40.88; H, 3.43; N, 11.92; Cl, 29.71%.

***N*-Acetyl-4-nitro-1-naphthylamine.** 4-Nitro-1-naphthylamine (2 g) dissolved in acetic anhydride (70 m*l*) was heated at 100°C for 2 hr. On cooling crystals formed, which were recrystallized from ethanol.

[*1] Presented at the International Conference on Photochemistry, Tokyo, August 28, 1965. This paper is a part of the Doctoral Thesis submitted by the author to the University of Tokyo, 1966.

1) Z. Koana, International Congress of Photographic Science, Tokyo (1967).

2) E. M. Robertson, W. P. Van Deusen, L. M. Minsk, *J. Appl. Polymer Sci.*, **2**, 308 (1959).

3) M. Tsuda, *J. Polymer Sci.*, **B2**, 1143 (1964).

4) M. Tsuda, *Makromol. Chem.*, **74**, 174, 183 (1964).

Mp 191.5—192°C. Found: C, 62.75; H, 4.44; N, 11.85%. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.16%.

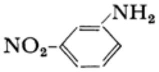
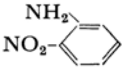
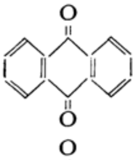
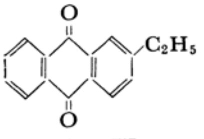
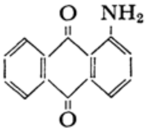
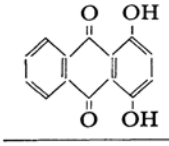
***N*-Benzoyl-4-nitro-1-naphthylamine.** 4-Nitro-1-naphthylamine (1.88 g) dissolved in methyl ethyl ketone (75 m*l*) and benzoyl chloride (1.55 g) were added to 10% aqueous NaOH solution (75 m*l*), and then vigorously agitated for 20 min. After standing, the upper layer was separated and methyl ethyl ketone was distilled off. The residue was recrystallized from ethanol. Mp 238—238.5°C. Found: C, 69.97; H, 4.37; N, 9.55%. Calcd for $C_{17}H_{12}N_2O_3$: C, 69.84; H, 4.14; N, 9.59%.

Other Substances. Guaranteed grade substances from Tokyo Kasei Co., Ltd. were recrystallized. Their melting points agreed with the literature values.

Sensitometry. Gray scale method proposed by Minsk *et al.*[7] was used. The gray scale used was a Kodak Step Tablet No. 2 calibrated by densitometer. The light source was a super high pressure mercury arc lamp (Toshiba SHL-100 UV). Picramide was used as a standard, assuming a relative sensitivity of 400.

Spectroscopy. Emission spectra were measured by a Hitachi EPM-2S type spectrometer, and absorption spectra were measured by Shimadzu IV-50 type spectrometer.

TABLE 1. EMISSION SPECTRA AND SENSITIVITY

Compound	Emission spectra[5,6]	Relative sensitivity
	P	410
	F	0
	F	0
	P	130
	P	360
	F	0
	F	0

P: phosphorescence, F: fluorescence

Emission Spectra and Sensitivity

Sensitizers of poly(vinyl cinnamate) may be phosphorescent. It is known that some compounds with similar structures to sensitizers do not sensitize. It was found that they do not phosphoresce but fluoresce as shown in Table 1. The failure to sensitize is easily understood in terms of the T-state mechanism, because, when step 2 in Fig. 1 does not occur, fluorescence only is observed and not phosphorescence.

Heavy Atom Effect

When heavy atoms are introduced into a molecule, step 2 of Fig. 1 is favored by the increase of the spin-orbit interaction. Therefore, we can expect an increase in the sensitizing effect of a sensitizer by the introduction of heavy atoms. At the same time the intensity of phosphorescence of the molecule is expected also to increase.

N,N-Dimethyl-4-nitroaniline is a sensitizer having a moderate sensitizing effect. It emits both fluorescence and phosphorescence rather strongly. Therefore, if heavy atoms are introduced into the molecule, we should obtain new sensitizers having

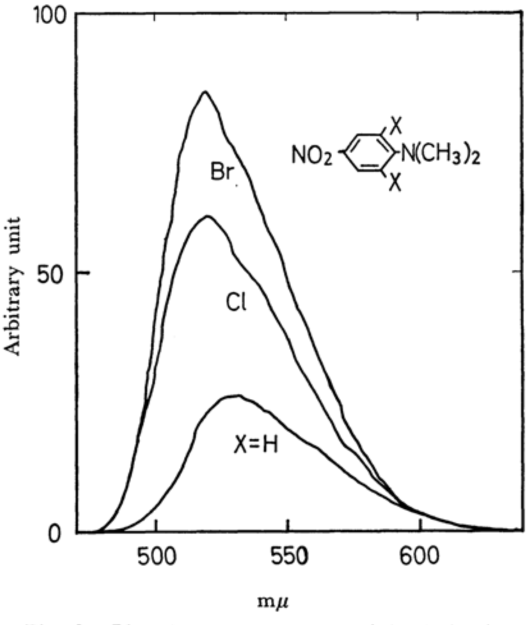


Fig. 2. Phosphorescence spectra of the derivatives of *N,N*-dimethyl-4-nitroaniline.
H: *N,N*-dimethyl-4-nitroaniline 1.004 mg/cc;
Cl: 2,6-dichloro derivative 1.001 mg/cc;
Br: 2,6-dibromo derivative 1.007 mg/cc;
Solvent: methanol 1 volume, methlcyclohexane 1, ethyl ether 1; Excitation 360 mμ (slit width 40 mμ); Analizer slit width: 2mμ.

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[5] R. Foster, D. Ll, Hammick, G. M. Hood and A. C. E. Sanders, *J. Chem. Soc.*, **1956**, 4865.

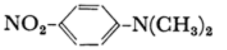
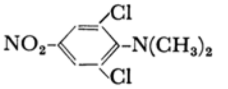
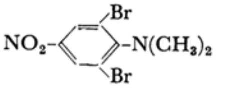
[6] H. H. Dearman and A. Chan, *J. Chem. Phys.*, **44**, 416 (1966).

[7] L. M. Minck, J. G. Smith, W. P. Van Deusen and J. F. Wright, *J. Appl. Polymer Sci.*, **2**, 302 (1959).

a strong sensitizing effect and showing strong phosphorescence. Phosphorescence spectra of *N,N*-dimethyl-4-nitroaniline (H), and its 2,6-dichloro (Cl), and 2,6-dibromo (Br) derivatives are shown in Fig. 2. The shapes of the spectra are very similar to each other.

It is noticed that the intensity of phosphorescence increases remarkably by replacing H with Cl, or with Br, and the sensitizing effect also increases as expected (Table 2).

TABLE 2. HEAVY ATOM EFFECT ON SENSITIZERS

Sensitizer	Relative sensitivity
	137
	561
	797

As the sensitizing effects are measured by the gray scale method using a super high pressure mercury are lamp as a light source, it may be considered that the exposure is due mainly to 365, 405 and 436 mμ lines considering the absorption spectra of these three sensitizers. The ratio of the intensities of these active lights emitting from the light source is 2.25 : 1 : 2.04, and the transmittances of the gray scale at those wavelengths are 55, 79, and 82%. With those corrections the relative yields of phosphorescence at these three wavelengths are obtained. The sum of the relative yields of phosphorescence at these three wavelengths plotted as the abscissa of Fig. 3 *vs.* the relative sensitivity as the ordinate produced a straight line. The relative sensitivity of the sensitizer is directly proportional to the relative yield of its phosphorescence within the limits of experimental error.

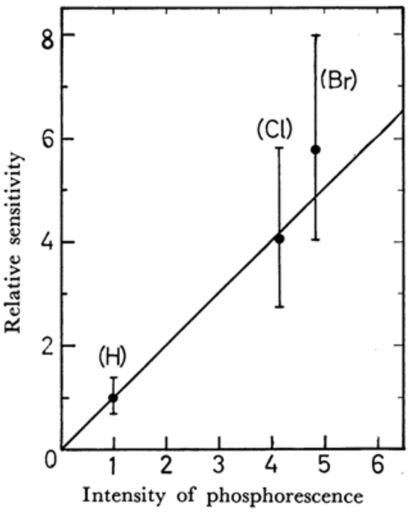


Fig. 3. Relationship between phosphorescence yields and relative sensitivities.

Energy of Triplet State

From the T-state mechanism, the sensitizing effect should be observed only when the energy of T_1 of the sensitizer is equal to or larger than that of the cinnamoyl group (Fig. 1). Therefore, there are some compounds which have not sensitizing effects in spite of their strong phosphorescence. For example, 4-nitro-1-naphthylamine phosphoresces strongly,$^{5)}$ and its chemical structure is similar to 4-nitroaniline and α-nitronaphthalene (both are strong sensitizers), but it has no sensitizing effect.

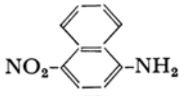
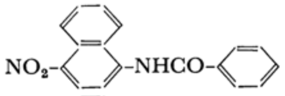
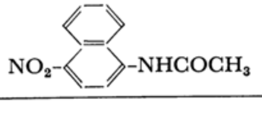
Compounds having similar chemical structures may have a constant value of the gap between the peaks of their absorption spectra and the 0–0 bands of their phosphorescence spectra. The values are, for example, about 6000 cm^{-1} for the analogues of 4-nitroaniline and about 10000 cm^{-1} for the analogues of 4-nitrodiphenyl as shown in Table 3. Using this phenomenon, we may expect to change a non-sensitizer, 4-nitro-1-naphthylamine, into a sensitizer.

The peak of the absorption spectrum of 4-nitro-1-naphthylamine shifts toward the shorter wavelength region by *N*-acylation; so, the energy of

TABLE 3. THE GAP BETWEEN THE PEAK OF ABSORPTION SPECTRUM AND THE 0–0 BAND OF PHOSPHORESCENCE SPECTRUM

Compound	Gap, cm^{-1}
4-Nitroaniline	7338
N-Methyl-4-nitroaniline	6576
N,N-Dimethyl-4-nitroaniline	6625
4-Nitro-1-naphthylamine	5956
4-Nitrodiphenyl	9262
4,4′-Dinitrodiphenyl	12343
2-Nitrofluorene	9703

TABLE 4. SENSITIZING EFFECT OF *N*-ACYL-4-NITRO-1-NAPHTHYLAMINES

Compound	Relative sensitivity
	0
	769
	1100

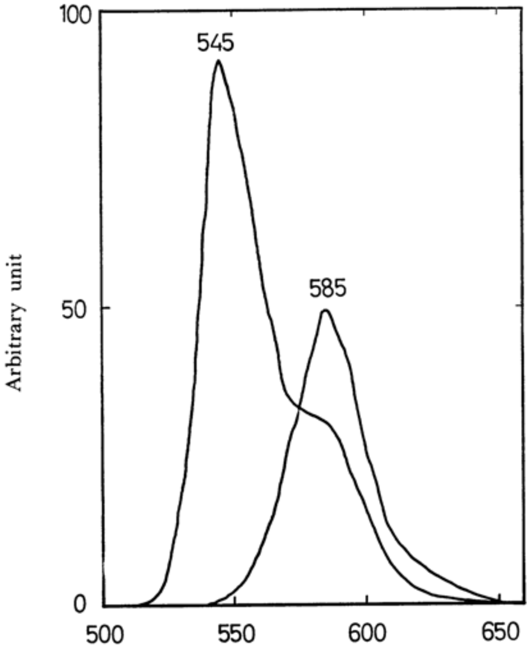


Fig. 4. Phosphorescence spectra of 4-nitro-1-naphthylamine (peak: 585 mμ) and *N*-acetyl-4-nitro-1-naphthylamine (peak: 545 mμ). Conditions in measurements are different.

T_1 of the *N*-acylated derivative may increase, and get into the sensitizing region. *N*-Acetyl-4-nitro-1-naphthylamine and *N*-benzoyl-4-nitro-1-naphthylamine have really been found to have a strong sensitizing effect (Table 4). The phosphorescence spectra of 4-nitro-1-naphthylamine and its *N*-acetyl derivative are shown in Fig. 4. *N*-Acetyl-4-nitro-1-naphthylamine emits far stronger phosphorescence than 4-nitro-1-naphthylamine though Foster reported[5] that the latter phosphoresces strongly. The excitation spectra of both of them measured under the same conditions are shown in Fig. 5.

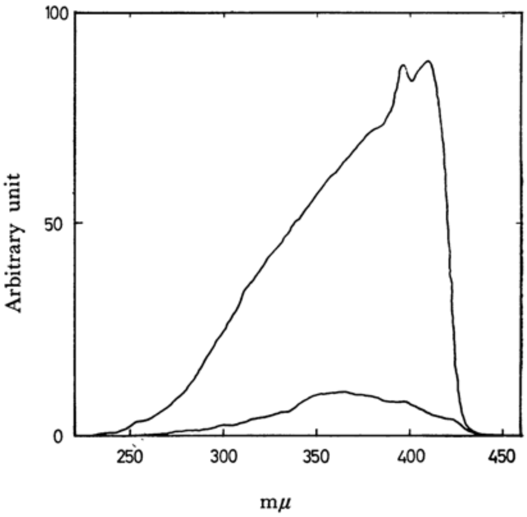


Fig. 5. Excitation spectra of 4-nitro-1-naphthylamine and *N*-acetyl-4-nitro-1-naphthylamine at the same conditions.
Analizer was set at the peak of Fig. 4. Figures of abscissa are the wavelength of excitation light. Conditions: *N*-acetyl-4-nitro-1-naphthylamine 0.944 mg/cc; 4-nitro-1-naphthylamine 0.957 mg/cc; Exciter slit width 3.5 mμ.

Conclusion

It is shown that some deductions from the T-state mechanism agree well with experimental facts. This strongly supports that the spectral sensitization of poly(vinyl cinnamate) occurs by the triplet energy transfer from sensitizers to the cinnamoyl group of the polymer. The theory is also useful for finding new sensitizers.