Redox Sensitization in the Photochromic Polymers of the Thionine Series

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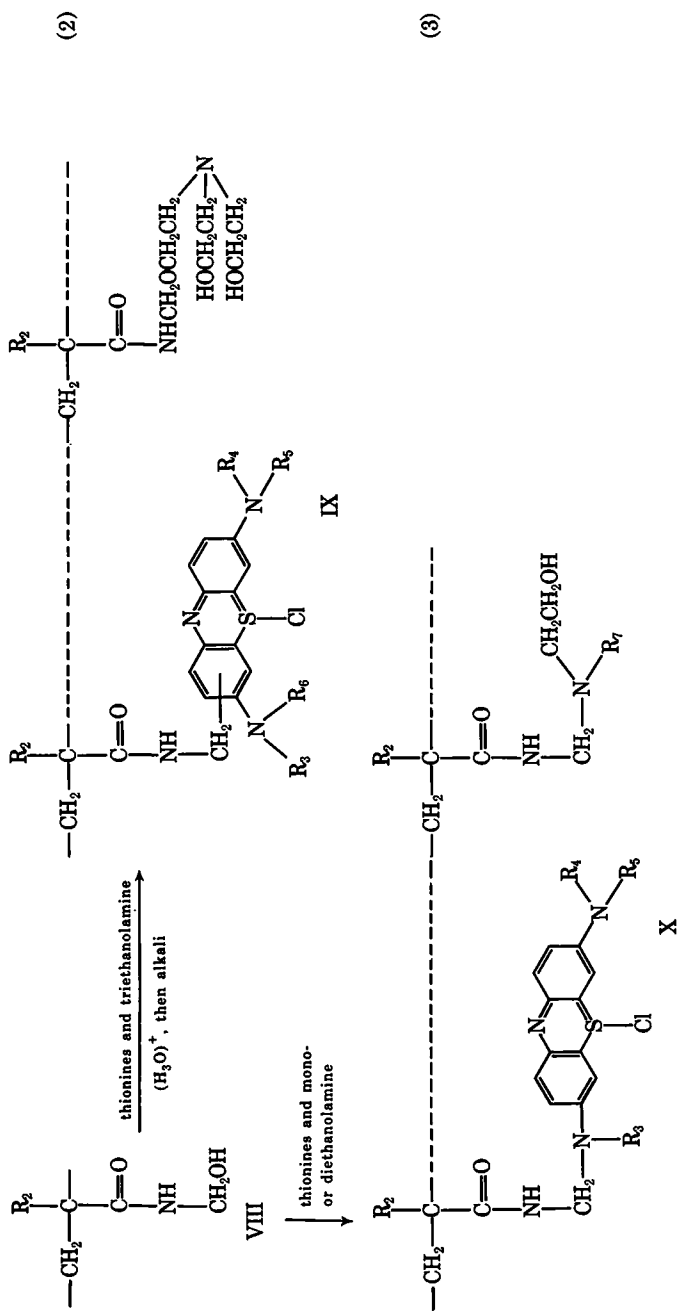
Synopsis

The incorporation of electron-donating components such as mono-, di-, and triethanolamines into the thionine photoredox system was tried (1) by copolymer preparations containing the acrylamidomethylthionines and triethanolamine monoacrylic ester as components, (2) by the reaction of triethanolamine and thionines with the N-hydroxymethyl group in polymer in an acid medium, and (3) by the reaction of mono- or diethanolamine and thionines with the N-hydroxymethyl group. The photochromic behavior of the resulting polymers were investigated. It was found that ethanolamine components incorporated into the polymer chain are as effective as their monomeric equivalents, to the extent that the sensitivity is among the highest so far investigated.

INTRODUCTION

In previous papers,[1,2] we have reported that vinyl polymers containing the thionine residue as side chain, when coupled with suitable electron donors such as ferrous ion, poly(vinyl alcoholic) and cellulosic hydroxyls, and some enzymes present reversible photobleaching of their characteristic blue colors. It has been principally postulated there that the thionine component as electron acceptor is reduced with an electron donor under illumination of light, which leads to the production of the colorless leuco form.

In a search for another effective photosensitizer, i.e., an electron donor for the thionine component, we have found that the ethanolamine residue incorporated into a vinyl polymer chain is as effective as its monomeric equivalent. Thus, a polymer system containing both the thionine and ethanolamine components forms an excellent blue film which quickly undergoes photobleaching under illumination of visible light, the rate of recovery being dependent upon the temperature and especially humidity of the atmosphere. Since, in the thionine photoredox system, both electron acceptor thionines and donors, e.g., ferrous ion, are water soluble, it is important also from a practical standpoint that these acceptor and donor components are linked to polymer chains via chemical bonds, thereby affording waterproofness to this system.

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In this paper will be reported the effects of the mode of the incorporation of the ethanolamine residue into the thionine polymer chain upon the reversible photobleaching behavior of the polymer. The incorporation of the ethanolamine residues was carried out according to the following three sequences:

$$
\begin{array}{c}
\underset{|}{R_1} \\
CH_2\!\!=\!\!\overset{|}{C}\!\!-\!\!COCl \quad + \quad (HOCH_2CH_2)_3N \quad \longrightarrow \\
I \qquad\qquad\qquad II
\end{array}
$$

$$
\begin{array}{c}
\underset{|}{R_1} \\
CH_2\!\!=\!\!\overset{|}{C}\!\!-\!\!COOCH_2CH_2 \quad\quad \overset{H}{} \\
HOCH_2CH_2\!\!-\!\!N^+Cl^- \\
HOCH_2CH_2 \\
III
\end{array}
$$

copolymerization with
$CH_2\!=\!C(R_2)CONH_2$ ⟶

$$
\begin{array}{cc}
\underset{|}{R_2} & \underset{|}{R_1} \\
-\!CH_2\!\!-\!\!\overset{|}{C}\!-\!----\!CH_2\!\!-\!\!\overset{|}{C}\!-------- \\
C\!=\!O & C\!=\!O \\
NH_2 & O\!-\!CH_2CH_2 \overset{H}{} \\
& HOCH_2CH_2\!-\!N^+Cl^- \\
& HOCH_2CH_2 \\
& IV
\end{array}
$$

$\xrightarrow[\text{alkali}]{HCHO}$

$$
\begin{array}{cc}
\underset{|}{R_2} & \underset{|}{R_1} \\
-\!CH_2\!\!-\!\!\overset{|}{C}\!-------\!-CH_2\!\!-\!\!\overset{|}{C}\!------- \\
C\!=\!O & C\!=\!O \\
NHCH_2OH & O\!-\!CH_2CH_2 \\
V & HOCH_2CH_2\!-\!N \\
& HOCH_2CH_2
\end{array}
$$

$\xrightarrow{\text{thionines (VI)}}$

$$
\begin{array}{cc}
\underset{|}{R_2} & \underset{|}{R_1} \\
-\!CH_2\!\!-\!\!\overset{|}{C}\!---------------\!CH_2\!\!-\!\!\overset{|}{C}\!------- \quad (1). \\
C\!=\!O & C\!=\!O \\
NH & O\!-\!CH_2CH_2 \\
CH_2\!-\!N & HOCH_2CH_2\!-\!N \\
R_3 & HOCH_2CH_2
\end{array}
$$

VII

R_1, R_2, R_3, R_4, R_5 = H or CH_3

(2)

(3)

VIII

thionines and triethanolamine
$(H_3O)^+$, then alkali

thionines and mono-
or diethanolamine

IX

X

$R_6 = H$ or CH_3
$R_7 = H$ or CH_2CH_2OH

EXPERIMENTAL

Triethanolamine Hydrochloride Monoacrylate
(Monomer III: R_1 = H)

Acryloyl chloride, 3 ml, freshly distilled, was added dropwise under ice cooling to a solution of 10 g anhydrous triethanolamine in 20 ml anhydrous acetonitrile with vigorous agitation; it took about 10 min. The solution with white precipitates was further stirred for 1 hr, followed by standing overnight at room temperature. The product was picked up by filtration with suction to provide 7.6 g of white crystals, mp 175°–177°C.

ANAL. Calcd for $C_9H_{18}O_4NCl$: C, 45.09%; H, 7.52%; N, 5.85%. Found: C, 45.51%; H, 7.48%; N, 5.53%.

The infrared spectrum by the KBr method presented the α,β-unsaturated ester C=O absorption at 1720 cm^{-1}, and an aqueous solution polymerization of this compound provided a water-soluble polymer, thereby indicating the absence of di- and triesters and giving the identification to the desired product.

The same procedure could be applied for the preparation of triethanolamine hydrochloride monomethacrylate (compound III: R_1 = CH_3) with the product of mp 174–176°C.

ANAL. Calcd for $C_{10}H_{20}O_4NCl$: C, 47.34%; H, 7.89%; N, 5.52%. Found: C, 47.52%; H, 7.61%; N, 5.44%.

Polymerization of Monomer III and Subsequent
Reactions to Afford Polymer VII

In a typical example, 0.5 g monomer III (R_1 = H), 5 g acrylamide, and 0.05 g potassium persulfate were dissolved in 100 ml water. The solution was heated in a small autoclave to 80°C for 90 min under nitrogen to provide a viscous polymer solution (IV) (pH 3) in almost quantitative yield. The viscous solution was treated with 10 g of an anion exchanger, Dowex 1-X8, to liberate the triethanolamine residue; 0.1 g paraformaldehyde was then added to the filtered solution, followed by stirring for 1 hr at 50°C. Azure A (VI), 0.05 g, was added to the resulting transparent solution (polymer V), followed by stirring at 70°C for 5 hr to provide polymer VII. The extent of reaction, as estimated according to the reductive titration with titanium trichloride for the aqueous solution of the product purified by repetitious precipitations into ethanol, was 62% based on the amido group in the polymer.

Preparation of Polymer IX

In a typical example, 0.8 g triethanolamine and 0.2 g paraformaldehyde were added to 8 g of 8% aqueous polyacrylamide (in trinsic viscosity 1 at 20°C) and the mixture was stirred at 50°C for 1 hr to effect the methylolation of the acrylamide component (pH 10). To the resulting colorless

transparent solution (VIII) was added 0.003 g thionine, the solution was stirred at 50°C for 30 min, and several drops of concentrated hydrochloric acid was added to regulate the pH value of the solution to ca. 5. Since this solution was insolubilized by the application of heat, it was applied onto the surface of a thin glass plate, followed by drying at 80°C for 30 min to prepare a blue-colored film, which was cured at 120°C for 15 min and allowed to stand overnight in a dilute aqueous potassium carbonate, followed by aqueous rinsings and subsequent drying to provide a blue film (IX). No elution of thionine was recognized by this procedure.

Preparation of Polymer X

A typical procedure is as follows: N-Hydroxymethyl acrylamide, 5 g, 10 g methyl methacrylate, 10 g butyl acrylate, and 0.2 g α,α'-azobisisobutyronitrile were dissolved in 75 ml ethanol. The solution was stirred at 80°C for 3 hr under nitrogen to afford a viscous polymer solution (VIII) in almost quantitative yield. To 10 ml of this polymer solution were added 0.2 g diethanolamine and 0.01 g azure A, followed by stirring first for 1 hr at 50°C, then for 8 hr under refluxing, with exclusion of light to afford polymer X, which was purified by repeated precipitations into water.

As the starting polymer, the methylolation product of a graft copolymer of acrylamide onto poly(vinyl alcohol), e.g., with ceric ammonium nitrate as initiator, can also be employed.

Preparation of Sample

Samples for spectral change determination were prepared by spreading polymer solutions over thin glass plates and drying to ca. 0.05 mm thickness. Drying at 80°C and subsequent curing ranging from 100° to 120°C were carried out when required. At least a week elapsed before measurement of photochromism.

Measuring Instrument

A Hitachi rapid-scan spectrophotometer (Model RSP-2) with a scanning time of ca. 0.15 sec from 220 to 700 nm and fitted with a 150-watt xenon lamp as radiation source was employed for the investigation of photochromic behavior.

RESULTS AND DISCUSSION

Effect of Radiation Wavelength

In Figure 1 are indicated typical spectral changes of polymer VII film with irradiation. The effect of radiation wavelength upon the rate of spectral change is also given in Table I. As is usual in the thionine photoredox system, the red light was the most effective for the rate of photobleaching in this case, too.
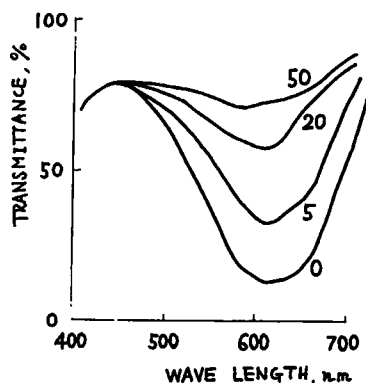
Fig. 1. Typical spectral change of polymer VII film at 8°C under irradiation of red light with maximum transmission at 700 nm.   Figures in the diagram denote irradiation times in seconds.   Polymer VII was prepared by grafting monomer III and acrylamide to poly(vinyl alcohol), followed by reaction with azure B, as described in text.

TABLE I
Effect of Radiation Wavelength Upon Rate of Spectral
Change at 8°C for Polymer VII Film[a]

Filter (max. transmittance)	Initial rate of decrease of 610 nm peak, sec^{-1}
Toshiba V-R63 (700 nm)	9.8×10^{-2}
Toshiba V-G52 (530 nm)	1.2×10^{-2}
Toshiba V-B46 (460 nm)	2.0×10^{-2}

[a] The same polymer as that in Fig. 1.   Radiation source: 150-watt xenon lamp.

Effect of Donor Concentration

Figure 2 indicates the effect of the donor (triethanolamine residue) concentration in the polymer on the initial fading rate at the absorption maximum which ranged from 600 to 640 nm, as compared with the data for those prepared in the same manner using triethanolamine hydrochloride monoacetate instead of monoacetate or monoacrylate.

These curves indicate that the introduction of the ethanolamine residue strongly improves the sensitivity of photochromism as compared with the polymers with poly(vinyl alcohol) alone.   They also indicate that no decisive improvement in the photoredox behavior is recognized for thionine polymers by the incorporation of the donor component to polymer molecules by chemical bond, except the physical stabilities obtained, such as lower migration ability and higher resistance to solvent extraction.

Effect of the Mode of Incorporation of Donor Component into Polymer

Table II indicates the effect of the mode of the incorporation of donor component into polymer.   It is apparent from this table that mode 2 is somewhat inferior to the rest.   This can be seen from the fact that acidic cures in the solid state are necessary in mode 2 in order to assure the reac-
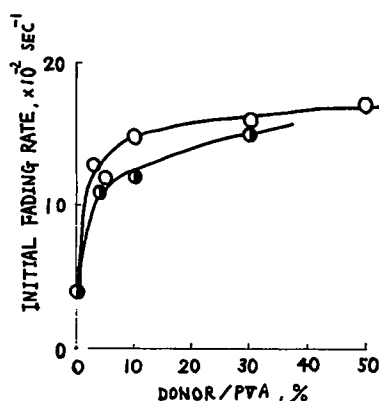
Fig. 2. Effect of donor concentration on initial fading rate of thionine polymer film at 8°C: (O) polymer prepared by graft polymerization of monomer III and acrylamide onto poly(vinyl alcohol) (PVA) with ceric ammonium nitrate and subsequent methylolation with formaldehyde, followed by the reaction with azure B; (◑) polymer prepared in the same manner as above, except that triethanolamine hydrochloride monoacetate was employed instead of monomer III.

tion of triethanolamine with N-hydroxymethyl group of polymer and subsequent alkali treatment would not remove acidic components completely, which lowers the ability of triethanolamine component as electron donor in the photoredox reaction.

The monoethanolamine component in mode 3 is not a good donor not only because it provides fairly low fading rates but also because of poor transparency of the film made thereof. Since it is known that thiazine dyes, such as methylene blue, are susceptible to association which might lead to photochemically inactive products,[3] the fixing of the thionine residue

TABLE II
Effect of Mode of Donor Incorporation Into Polymer

Mode	Acceptor component	Donor component[a]	Absorption maximum, nm	Initial fading rate, sec^{-1}
1	azure B	triethanolamine acrylate	630	$16.5 \times 10^{-2}(8°)$
	azure B	triethanolamine methacrylate	620	$16.1 \times 10^{-2}(8°)$
2	thionine	triethanolamine	610	$10.4 \times 10^{-2}(5°)$
	azure B	triethanolamine	600	$9.3 \times 10^{-2}(5°)$
3	thionine	monoethanolamine	620	$12.1 \times 10^{-2}(5°)$
	thionine	diethanolamine	610	$17.1 \times 10^{-2}(5\ )$
	thionine	diethanolamine	610	$17.1 \times 10^{-2}(5°)$
b	azure B	triethanolamine monoacetate	630	$12.9 \times 10^{-2}(8°)$

[a] 15 weight-%/polymer in film state.
[b] Donor was mixed.

to a vinyl polymer chain might also prevent this association to bring about better photoredox behavior.

Role of the Ethanolamine Residue in Photobleaching

The exact mechanism of the role of the ethanolamine residue in the photobleaching of the thionine residue in polymer is not clear. However, judging from the role of triethanolamine in the methylene blue–triethanolamine photoredox initiation in vinyl polymerization[3] and ready oxidation of ethanolamines effected with conventional oxidizing agents, such as bromine and ceric ion, a photoredox mechanism which proposes that the photoactivated thionine residue attacks the ethanolamine residue to oxidize the latter appears to be plausible. The dark reaction, i.e., color recovery, on the other hand, appears mainly to take place by air oxidation of the reduced colorless thionine residues.

Moreover, since the thionine cations are involved in this photoredox system, their hydration appears to be important to assure smooth progress of both light and dark reactions, so that the rates of both reactions in the film state, especially in dark, are remarkably influenced by the moisture content, i.e., humidity of the atmosphere.

References

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