

Photomodification of Polymer Surfaces: Photoreaction of Thiocyanato Group-Bearing Polymers

In previous papers,^{1,2} the photorearrangement and subsequent intramolecular cyclization of thiocyanatoacetyl groups in a polymer matrix were described and a new image-forming process based on the selective dyeing of the polymer film was proposed.

However, in the course of further investigation, we noticed that the dyeing behavior of 100% thiocyanato group-substituted polymer film was quite different from those of partially substituted (20%, 50%, and 70%) polymer films. The latter was not dyed at all in the intact state, but dyed well after UV irradiation. On the other hand, the former was dyed well with cationic dyes in the intact state and became difficult to dye after UV irradiation. Therefore, the dyeing behavior of the former which is the main subject of this work was termed "a reverse dyeing behavior" for convenience. Clarification of the mechanism of this phenomenon would be of value from the viewpoint of photomodification of the surface of polymer film.

In this paper, in order to clarify the mechanism for the reverse dyeing behavior of the polymer films, each step of bromination and of thiocyanation was studied in detail in connection with the dyeing behavior of the resulting polymer films.

EXPERIMENTAL

Syntheses of Low-Molecular Weight Model Compounds

ω,ω -Dibromoacetophenone was prepared by the method of Neville³: mp 31–32°C (lit. 35–36°C).

ANAL. Calcd for $C_8H_6Br_2O$: H 2.18%; C 34.57%. Found: H 1.92%; C 34.64%.

ω,ω -Dithiocyanatoacetophenone. 2.1 g (21.6 mmol) of potassium thiocyanate dissolved in 12 mL of DMF was added to 3.0 g (10.8 mmol) of ω,ω -dibromoacetophenone dissolved in 15 mL of DMF and the solution was stirred for 3 h at room temperature. After filtering off potassium bromide precipitated, the filtrate was poured into water. The product was obtained as a brownish precipitate and recrystallized from chloroform. Yield: 1.3 g (51.4% of theoretical), decomp. above 120°C.

ANAL. Calcd for $C_{10}H_6N_2OS_2$: H 2.58%; C 51.26%; N 11.96%. Found: H 1.93%; C 51.37%; N 11.50.

IR: 1680 cm^{-1} ($\nu_{C=O}$); 2150 cm^{-1} (ν_{SCN}).

Mass: M^+ , 234; $M-27$ (HCN), 207.

Synthesis of Polymers

Several kinds of bromine-substituted polymers, for example, poly[4-bromoacetylstyrene(85)-co-4-dibromoacetylstyrene(15)] (115%-PBAS), were prepared from poly(4-acetylstyrene) by the same method as described before^{1,2} except for the conditions of bromination (i.e., the amount of bromine, reaction time, and reaction temperature).

Poly(4-dibromoacetylstyrene) (200%-PBAS) was prepared using double molar amounts of bromine illuminated by visible light using a photo flood lamp (National PRS-300W REF lamp).

ANAL. Calcd for $C_{10}H_8OBr_2$: H 2.65%, C 39.51%. Found: H 2.45%, C 39.65%.

The 115%-PBAS and 200%-PBAS were reacted with potassium thiocyanate in DMF as described earlier, and the resulting polymers were abbreviated as 115%-PTCAS and 200%-PTCAS, respectively.

ANAL. For 200%-PTCAS: H 2.59%; C 52.28%, N 8.35%.

The degree of substitution of bromine atom by thiocyanato group was calculated from the results of elemental analysis to be 80–85% and was in good agreement with our previous data.

Photoreaction and Dyeing of Polymer Films

Films were prepared by casting from a polymer solution in tetrahydrofuran or in DMF-methyl ethyl ketone mixture (1:2 by volume) onto a polyester film (80 μm thickness) and were irradiated with a medium pressure mercury lamp, USHIO-UM 102, for a given time in air.

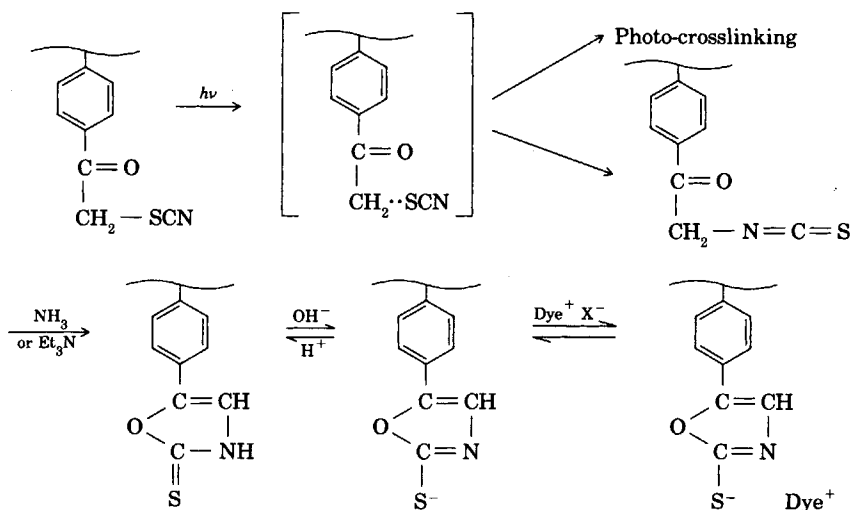
The irradiated films were dyed by dipping these into a dye bath [0.2 wt % fuchsine in methanol-dioxane (9:1 by volume)] for 10 s after pretreatment with a methanolic solution of CH_3ONa (0.1 wt %) instead of using an alkali-containing cationic dye bath, because alkali precipitates the cationic dye from the bath.

Measurement

IR spectra were recorded on a Hitachi 215 Grating Infrared Spectrophotometer. UV spectra were recorded on a Shimadzu Double Beam UV-200S Spectrophotometer. NMR spectra were measured on a Hitachi R-24A High Resolution NMR Spectrometer. Elemental analysis was performed by a Yanaco MT 2 CHN Corder. ATR-IR spectra were recorded on a Nicolet 7199 FT-IR Spectrophotometer.

RESULTS AND DISCUSSION

In our previous paper,² we reported that the irradiated parts of 20%; 50%; or 70%-PTCAS films could be dyed selectively with several kinds of cationic dyes and that the amount of dye adsorption increased with increasing irradiation time. The mechanism of dyeing was found to be as follows:



However, the dyeing behavior of 100%-PTCAS films is quite different from that of 20%-PTCAS films. Contrary to 20%-PTCAS films, it was well dyed with cationic dyes in an alkaline dye bath and did not dye at all after irradiation with UV light. In Figure 1, the absorbances at 555 nm of the dyed 115%-PTCAS films are plotted as a function of irradiation time. Figure 1 shows that the film does not dye at all within a few minutes when irradiated with UV light.

As this difference in dyeing behavior arises from the surface characteristic of the polymer films, we studied the functional groups on the surface of the films by means of ATR FT-IR spectroscopy.

From the fact that, in the reaction of halides with metal thiocyanate, both thiocyanate and isothiocyanate can be formed depending upon the halide structure and reaction conditions,⁴ it would easily be expected that the partially formed isothiocyanatoacetyl groups play a role in dyeing the polymer films. However, this possibility can be excluded by the absence of absorption band at around 2050 cm^{-1} (ν_{NCS}) in the ATR IR spectrum in Figure 2(b).

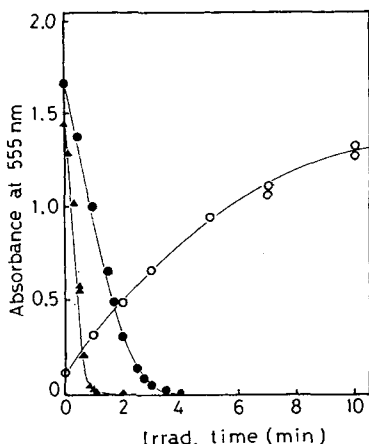


Fig. 1. Adsorption of fuchsin on the polymer films irradiated with UV light: (○) 20%-PTCAS, $\lambda > 310$ nm; (●) 115%-PTCAS, $\lambda > 310$ nm; (▲) 115%-PTCAS, $\lambda > 200$ nm.

In Figure 3(a), the absorption bands at 2060 cm^{-1} (ν_{NCS}), 1227 cm^{-1} , and 985 cm^{-1} appear upon UV irradiation, and these bands coincide in position with those in the transmission IR spectrum. This fact would provide a strong evidence for the mechanism (scheme 1) of photochemical reactions in 20%-PTCAS films. However, in Figure 3(b), an absorption band is observed at 1992 cm^{-1} on irradiation with UV light ($\lambda > 310$ nm). This large shift to a longer wavelength region is considered to originate from a chromophore different from NCS group.

The polymers used in this experiment were prepared by bromination and subsequent thio-cyanation of PAS. However, the reverse dyeing behavior was observed only in the polymer films which had been brominated with an amount of bromine equal to or greater than 4-acetylstyrene units.

It is already known that dibromo-substitution can easily occur when the reaction mixture is irradiated with visible light in the bromination step.³ Kröhnke⁵ also reported the formation of ω,ω -dibromoacetophenone even in the reaction of acetophenone with an equimolar amount of bromine.

Table I lists the UV and $^1\text{H-NMR}$ spectral data of the polymers prepared and of their low-molecular weight model compounds. The red shift of λ_{max} in UV absorption spectra is observed by introducing two substituent groups both in the model compounds and polymers. The chemical shifts of labile methylene or methine protons in polymers are also consistent with those

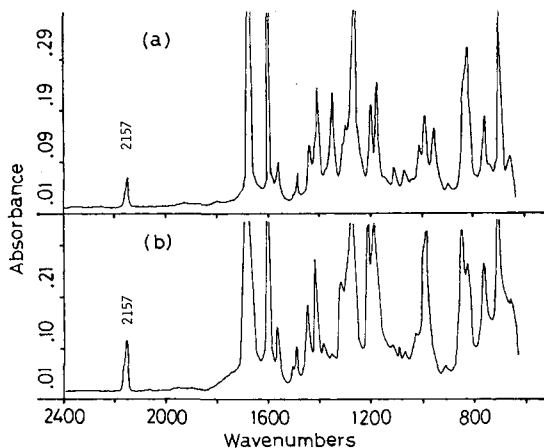


Fig. 2. ATR FT-IR spectra of the polymer films before UV irradiation. * Wilks ATR type 50, NSD = 400: (a) 20%-PTCAS; (b) 100%-PTCAS.

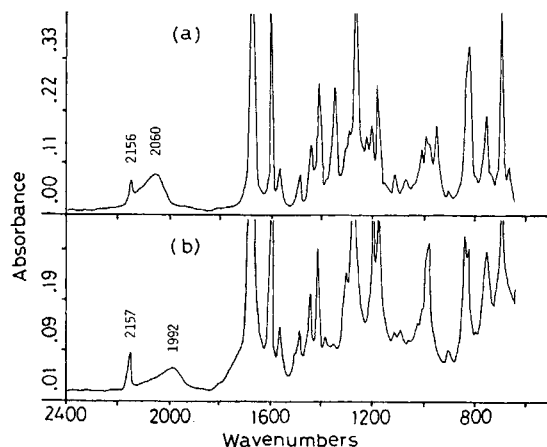


Fig. 3. ATR FT-IR spectra of the polymer films after UV irradiation. * Wilks ATR type 50, NSD = 400: (a) 20%-PTCAS; (b) 100%-PTCAS.

in the model compounds. It can, therefore, be said that the same reaction is occurring in the polymer as in the low-molecular weight model compounds. The same can be said from comparison of the IR absorption bands in the 1300 cm^{-1} (δ_{CH_2})– 1000 cm^{-1} region.

From the results above, one can easily expect that the partial dibromo-group substitution and subsequent dithiocyanato group substitution of PAS may occur during the synthesis of 100%-PTCAS. So we studied the relationship between the formation of the dithiocyanatoacetyl groups and the dyeing behavior of the polymer films.

Figure 4 shows the IR spectral changes in the $2200\text{--}1900\text{ cm}^{-1}$ region on UV irradiation of 115% (or 200%)–PTCAS films and of their model compounds. In the earlier stage of the photoreaction, an increase in absorbance at wavenumbers below 2000 cm^{-1} is observed in Figures 4(a) and 4(b). It was also found that the polymer films exhibiting the IR spectral change of this type showed a reverse dyeing behavior.

As shown in Figure 4(c), the IR spectral change of ω,ω -dithiocyanatoacetophenone in a polystyrene matrix is identical to that of 115%- or 200%-PTCAS but quite different from that of ω -thiocyanatoacetophenone, which shows absorption increase at 2045 cm^{-1} on UV irradiation [Fig. 4(d)]. It is apparent from these results that the reverse dyeing behavior of 100%-PTCAS

TABLE I
UV and $^1\text{H-NMR}$ Spectral Data

	UV		$^1\text{H-NMR}$
	λ_{max}	(log ϵ)	δ (ppm) ^b
$\phi\text{-COCH}_3$	240	(4.11) ^a	2.51
$\phi\text{-COCH}_2\text{Br}$	248	(3.98) ^a	4.85
$\phi\text{-COCH}_2\text{SCN}$	245	(4.16) ^a	5.00
$\phi\text{-COCHBr}_2$	257	(4.03) ^a	7.75
$\phi\text{-COCH(SCN)}_2$	256	(4.00) ^a	7.27
115%-PBAS	268 ^c		4.70
115%-PTCAS	267 ^c		—
200%-PBAS	277 ^c		7.55 ^d
200%-PTCAS	282 ^c		—

^a In methanol.

^b Methylene or methine protons, in DMSO-d_6 .

^c In film.

^d Overlapped with benzene ring protons.

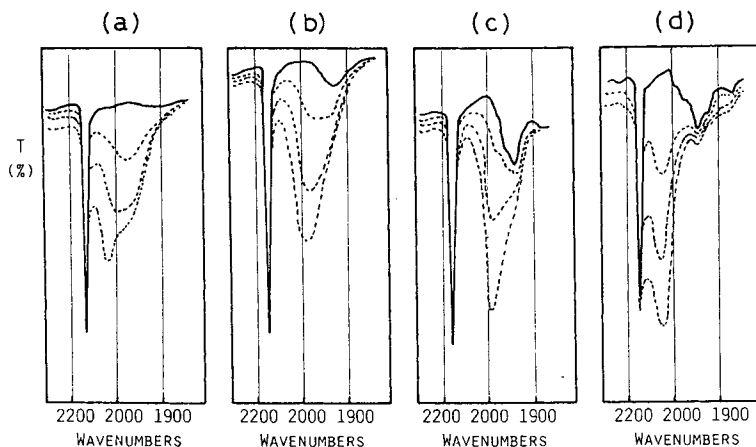


Fig. 4. IR spectral changes in the 2200–1900 cm^{-1} region upon irradiation with UV light ($\lambda > 310 \text{ nm}$): (a) 115%-PTCAS; (b) 200%-PTCAS; (c) $\phi\text{-COCH(SCN)}_2$ in PSt; (d) $\phi\text{-COCH}_2\text{SCN}$ in PSt.

films is due to the existence of dithiocyanatoacetyl groups formed during the bromination and subsequent thiocyanation of poly(4-acetylstyrene).

The facts that an alkali treatment was essential for dyeing of the polymer films and that the alkali-treated films were not dyed at all on neutralizing with HCl suggest the formation of anionic species as well as the specific reactivity of this functional group to an alkali.

It is well known that ω,ω -dibromoacetophenone is easily transformed into mandelic acid through the intermediate formation of phenylglyoxal in the presence of alkali.^{3,6} The spectral change of a methanolic solution of ω,ω -dibromoacetophenone with alkali treatment is very simple as shown in Figure 5(a). However, ω,ω -dithiocyanatoacetophenone ($1.5 \times 10^{-4} M$) in methanol shows a characteristic UV spectral change on addition of a small amount of an aqueous alkali, as shown in Figure 5(b). An aqueous alkali solution of this compound at a high concentration colored deep red, and this solution was neutralized with HCl and extracted with chloroform. From the results of the quantitative analysis of SCN^- in the aqueous layer, it was found that one SCN group in the ω,ω -dithiocyanato group was liberated as a SCN anion.

Early in the 1920s, the reactions of acetyl thiocyanate with acid or alkali were studied extensively,⁷⁻⁹ and Weygand et al.,¹⁰ who studied the reaction of α -haloketone with potassium

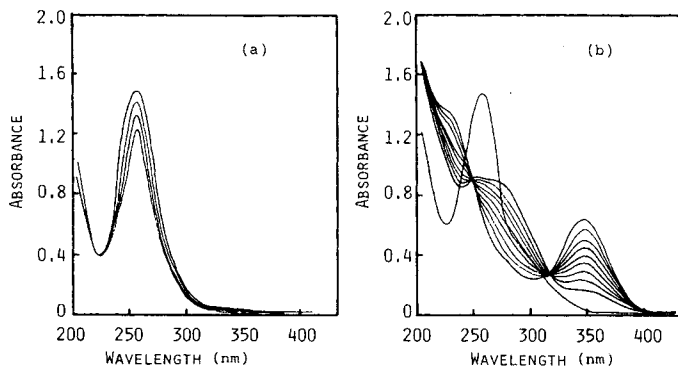
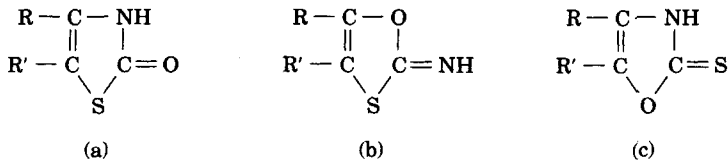
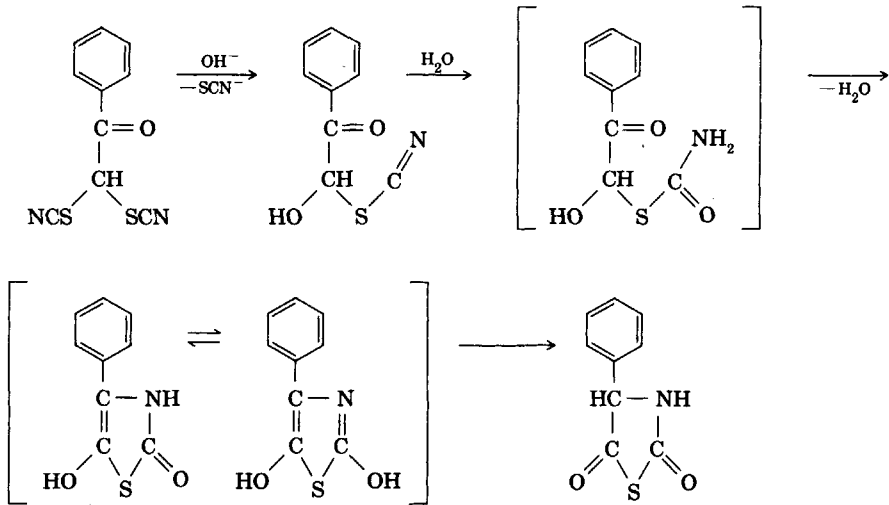


Fig. 5. UV spectral changes of methanolic solutions of acetophenone derivatives which were measured at about 1-min intervals after addition of a small amount of aqueous NaOH: (a) ω,ω -dibromoacetophenone ($1.4 \times 10^{-4} M$); (b) ω,ω -dithiocyanatoacetophenone ($1.5 \times 10^{-4} M$).

thiocyanate proposed the following three possible structures for the reaction products: (a) thiazolone-(2); (b) 2-imino-1,3-oxathiole; (c) oxazole-2-thione.



Using the ideas of Weygand, the mechanism can be written as follows:



On the other hand, the possibility of the formation of some resinous materials cannot be excluded from the concentration dependence of UV spectral change and from the results of IR spectroscopy and thin layer chromatography of the products obtained.

In this study, the complete isolation and characterization of the products were unsuccessful, and the detailed mechanism is not clear. However, it can be concluded from the specific reactivity of ω,ω -dithiocyanatoacetophenone to an alkali and the blue shift of UV absorption λ_{max} in the earlier stage of photoreaction of 200%-PTCAS films (Fig. 6) that the reverse dyeing

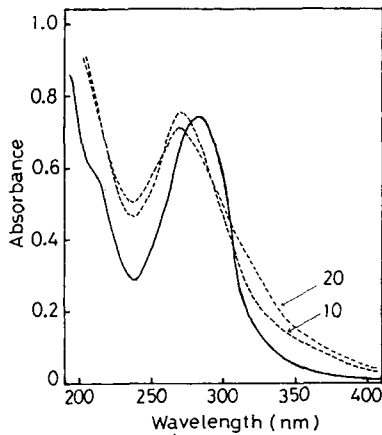


Fig. 6. UV spectral change of 200%-PTCAS film coated on a quartz plate upon UV irradiation ($\lambda > 310$ nm). Irradiation time: 20 min, 10 min.

behavior of 100%-PTCAS film originates from the existence of dithiocyanatoacetyl groups in the polymer.

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