

# Mechanism of Accelerated Photofading of Thioether Anthraquinone Dyes in Styrene Butadiene Resins\*

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## Synopsis

Many anthraquinone dyes fade in visible light up to 100 times faster in styrene butadiene copolymers than in polyester resins or polystyrene. A mechanistic investigation of the photofading of 1,5-dihydroxy-2,6-diisobutyl-4-thiophenylanthraquinone has established that the dye sensitizes formation of singlet oxygen, a very reactive species, which attacks the double bonds in the styrene butadiene, resulting in extensive chain cleavage and peroxide formation. The major process is the oxidation of the polymer, and the dye fading is a minor process whereby the dye is apparently attacked by polymeric peroxides. The mechanism appears to be general for anthraquinone dyes, especially those with thioether, amino, hydroxy, or double-bond functionality. Unfortunately the fading is unaffected by most antioxidant stabilizers: the best result achieved was a doubling of half-life with 1 wt% Spinuvex A-36. This is still insufficient to give colored styrene butadiene copolymer resins the intrinsic dye stability available in other polymers, rendering styrene butadiene unsuitable for applications requiring high photostability of anthraquinone dyes.

## INTRODUCTION

Anthraquinone dyes are common resin colorants because they are relatively easy to prepare. The color may be tuned from yellow to blue by appropriate choice of substituents on the aromatic ring system and they are relatively photostable. Further substitution on amino or thiophenyl groups may also be varied to fine tune the absorbance maximum. For example, a series of 1,5-dihydroxy-2,6-diisobutyl-4-thiophenylanthraquinones of general structure I (Fig. 1) was recently prepared with  $\lambda_{\max}$  varying from 498 to 518 nm.<sup>1</sup>

In exploratory investigation of the lightfastness properties of these and other yellow, red, magenta, and blue anthraquinone dyes in various polymer films, we observed in every case that the dyes were most photostable in polystyrene or styrene *n*-butylmethacrylate copolymer; somewhat less stable in polyester resins; and the least stable in styrene butadiene copolymer (Table I). While variations in fading rates of dyes in different polymers are known phenomena, most of the literature work has focused on cellulose.<sup>2-4</sup> The reason for the accelerated photofading in styrene butadiene is not obvious, although the presence of double bonds in styrene butadiene copolymer can be

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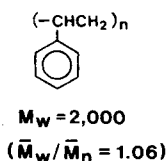
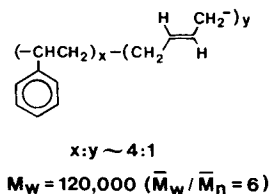
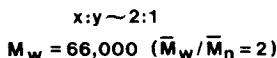
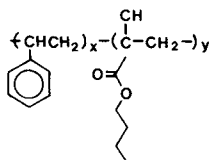
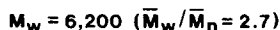
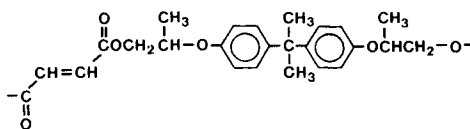
**Polystyrene****Styrene Butadiene****Styrene *n*-Butylmethacrylate****Polyester**

Fig. 2. Polymer structures and compositions employed in this investigation.

**EXPERIMENTAL****Resins**

The following resins were employed in this study: polystyrene (Pressure Chemical Corp.); styrene butadiene copolymer (Pliolite); styrene *n*-butylmethacrylate copolymer; and poly-[4,4'-dipropoxy-2,2-diphenylpropane fumarate] polyester (Scientific Polymer Products). The structures and compositional data for these resins are shown in Figure 2. All had glass transition temperatures of approximately 55°C.

**Synthesis and Preparation of Dyed Films**

The synthesis of the thioether anthraquinones by reaction of aromatic thiolates with 1,5-dihydroxy-2,6-diisobutyl-4-nitroanthraquinone has been described previously.<sup>1</sup>

Coating solutions were prepared by dissolving polymer (500 mg), recrystallized dye (15 mg), and additive (if any) in  $\text{CH}_2\text{Cl}_2/\text{ClCH}_2\text{CH}_2\text{Cl}$  (7:3 v/v; 25 mL). Films were cast on Mylar strips with a modified Gardner mechanical drawdown coater (speed:  $2.54 \text{ cm s}^{-1}$ , gap: 5, 10, 15, but typically 5 mil). The films were dried in a hood for several hours, then in a vacuum oven at 45°C overnight. Film samples ( $4.5 \times 5.0 \text{ cm}$ ) of uniform optical density (usually 0.5 to 0.8) were cut for the fading experiments. Film thickness was measured with a UPA Dermatron D-9 coating thickness tester equipped with a UPA SLG-1 probe calibrated against a 23.6  $\mu\text{m}$  GSIC thickness standard.

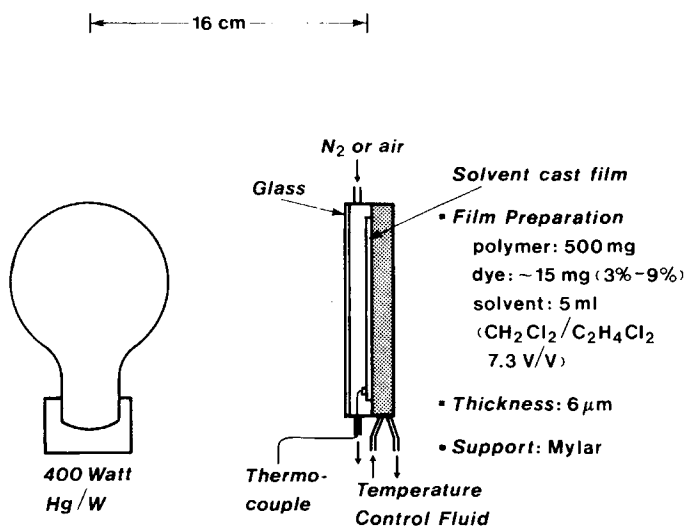


Fig. 3. Schematic of the Microscal lightfastness tester.

### Microscal Lightfastness Tester (Fig. 3)

The films were mounted in the glass-fronted, thermostatted cell holders in the Microscal Mark IV testing unit from Microscal Ltd (London, UK). The light source was a 400 W MB/U mercury/tungsten lamp (emission spectrum in Ref. 2). A thermocouple wire was taped to the front of the hold-down clip in the exposure cell to measure the film surface temperature. Coolant was circulated through the cell holder backs to provide a steady temperature. The temperature control of the film surface was  $\pm 3^\circ\text{C}$ . Without coolant circulation, the film surface temperature could rise as high as  $60\text{--}70^\circ\text{C}$ . The cells were left open to air unless an oxygen-free atmosphere was required, in which case, nitrogen was flowed through the cell, over the film at  $\sim 100\text{ mL/min}$ . During a typical fading experiment, each film sample was removed 10–30 times for a visible absorption spectrum measurement, referenced to pure polymer on Mylar, using a Hewlett Packard HP 8450A diode array spectrometer. Due to variations in film uniformity, the absorbance measurements were reproducible to  $\sim 3\%$ . The spectroscopic monitoring technique was non-destructive, except in the experiments in which polymer molecular weights were obtained during the run.

### Polymer Molecular Weight Measurements

In cases where gel permeation chromatograms (GPC) of film samples were required, small pieces of the film ( $\sim 50\text{ mm}^2$ ) were cut out and the colored layer dissolved off the Mylar with  $\text{CH}_2\text{Cl}_2$  (5 mL). This solution was concentrated to  $\sim 0.5\text{ mL}$  and subjected to GPC analysis (Instrument: Varian 8500 LC. Columns: Waters  $\mu$ -Styragel 100, 500,  $10^3$ ,  $10^4$ ,  $10^5$  Å pore size. Solvent: THF at 80 mL/h. Detector: HP 8450A spectrometer set to 254 nm). Molecular weights were determined using monodisperse polystyrene standards from Pressure Chemical.

### Isolation and Characterization of the Sulfoxide **IIa**

A film of styrene butadiene copolymer containing 3% by weight red dye **Ia** was faded at 63°C under standard conditions for 25 h. The faded portion of the film ( $\sim 3.0 \times 1.5$  cm) was cut out, and the sample dissolved off the Mylar with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25$  mL). These organics were concentrated to 1 mL, and applied to a preparative TLC plate (500  $\mu\text{m}$  thick silica gel,  $20 \times 20$  cm). The plate was eluted with hexane/acetone 4:1, and the yellow band isolated by extraction from the silica gel zone with MeOH (25 mL) and evaporation of the solvent.

The structure **IIa** was assigned to the yellow amorphous solid on the basis of the nuclear magnetic resonance (NMR), infrared (IR), and mass spectra.  $^1\text{HMR}$  ( $\text{CDCl}_3$ ): 2 isobutyl groups, 8 aromatic protons, and 2 exchangeable OH. The  $^1\text{HMR}$  of dye **IIa** differs from that of dye **Ia** primarily in the anthraquinone proton ortho to the sulfide: 6.8 ppm in **Ia** and 7.42 ppm in **IIa**, consistent with oxidation of sulfur to either a sulfone or a sulfoxide. Both the mass spectrum ( $\text{P}^+ 458$ ) and the IR spectrum of **IIa** ( $\text{S}=\text{O}$  band at  $1055\text{ cm}^{-1}$  in KBr) were characteristic of sulfoxide. Compound **IIa** was also obtained by benzoyl peroxide oxidation of **Ia** in toluene at 90°C for 24 h.

## RESULTS AND DISCUSSION

We evaluated the lightfastness of 1,5-dihydroxy-2,6-diisobutyl-4-thiophenylanthraquinone (**Ia**) with a series of solvent cast films in a Microscal lightfastness tester (Fig. 3), as described in more detail in the Experimental section. Four polymer resins were employed, as shown in Figure 2: polystyrene, styrene *n*-butylmethacrylate copolymer, the polyester 4,4'-dipropoxy-2,2-diphenylpropane fumarate, and styrene butadiene copolymer. Exposing the films through glass with the Hg/W lamp gave a visible light intensity approximately equal to one-third sun (according to the manufacturer) under conditions of controlled atmosphere and temperature. The changes in the visible absorption spectra of the films were monitored spectroscopically with a diode array spectrometer. There was no measurable fading in any polymer when the sample film was flushed with nitrogen throughout the experiment.

### Results

When styrene butadiene films of red dye **Ia** were subjected to visible radiation at 25° in air, there was a gradual bleaching in the intensity of the 516 nm band over 250 hours, as shown in Figure 4. Concurrent with this, a smaller new absorbance at 450 nm increased with time, and there were some minor changes between 300–400 nm. A parallel experiment in styrene *n*-butylmethacrylate copolymer resulted in very little change over 250 h.

By increasing the temperature to 63°C, the fading was somewhat different. At this temperature, more of the 450 nm product was observed, as shown in Figure 5. In the first 20 h, the 516 nm dye converted into the 450 nm species, and there was an isobestic point at 484 nm. The net effect was for the red film to become yellow. As the exposure continued at the higher temperature, the new yellow band also faded, to yield a large increase in the 300–400 nm absorbance (degraded polymer). The yellow product absorbing at 450 nm was isolated and characterized as the sulfoxide oxidation product **IIa**.

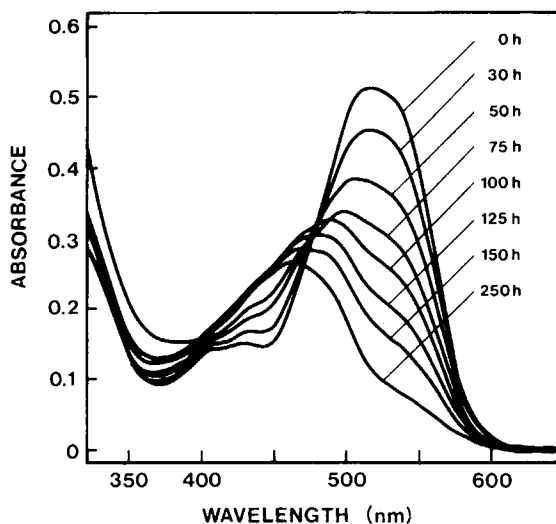


Fig. 4. Fading of red dye Ia in styrene butadiene at 25°C in air.

Figure 6 shows the GPC curves obtained from small samples of the film faded for Figure 5. At the beginning of the experiment, the GPC peak maximum corresponds to a nominal molecular weight ( $\bar{M}_p$ ) of 38,000 ( $\bar{M}_n$  16,000,  $\bar{M}_w$  120,000). After 19 hours of exposure, the first stage of the photofading was complete, the red dye had been converted to yellow, and the

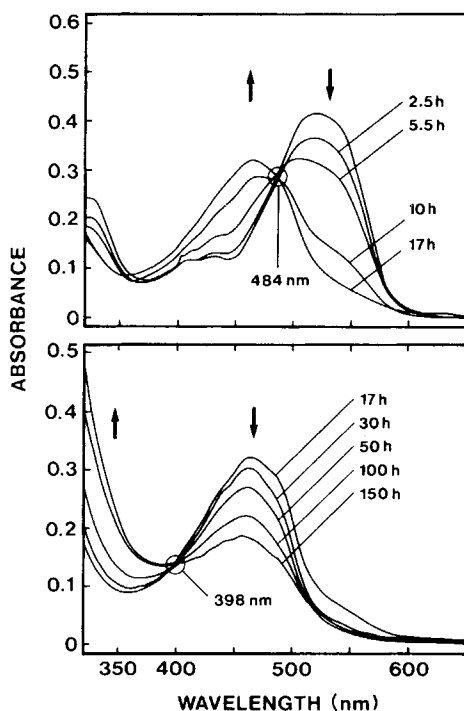


Fig. 5. Fading of red dye Ia in styrene butadiene at 63°C in air.

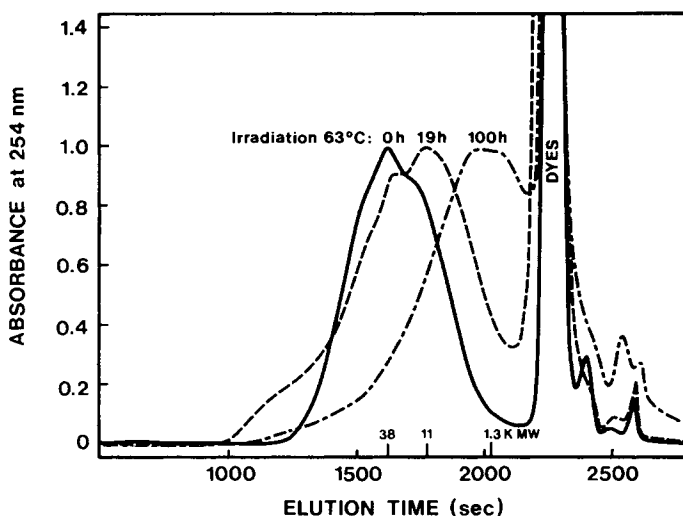


Fig. 6. GPC chromatograms for fading of red dye Ia at 63°C in styrene butadiene.

$M_p$  had dropped to 11,000. The GPC shows some high molecular weight polymer, indicating that some crosslinking occurred, in addition to the chain scission, and that both occurred simultaneously with dye fading. Upon continued exposure, the yellow dye also faded, with further polymer degradation, and catastrophic consequences for the molecular weight. Control experiments with unexposed pieces of the same dyed film, or with exposed undyed styrene butadiene copolymer resin, or with dyed styrene *n*-butylmethacrylate copolymer films, all showed no measurable change in the GPC polymer profile after 250 h at 63°C.

Ultraviolet (UV) spectra were obtained during the GPC runs and are presented for styrene butadiene copolymer in Figure 7: the degraded polymer

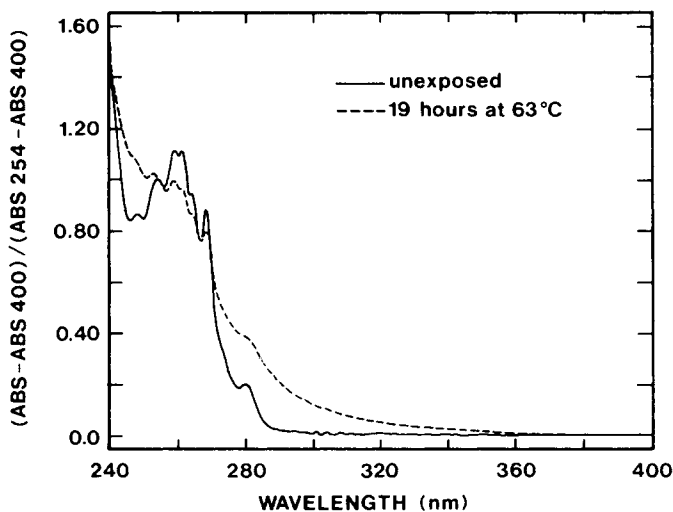


Fig. 7. Normalized UV spectra obtained at 1600 s during GPC runs shown in Figure 4 for the virgin red film (solid line) and after 19 h exposure at 63°C (dashed line).

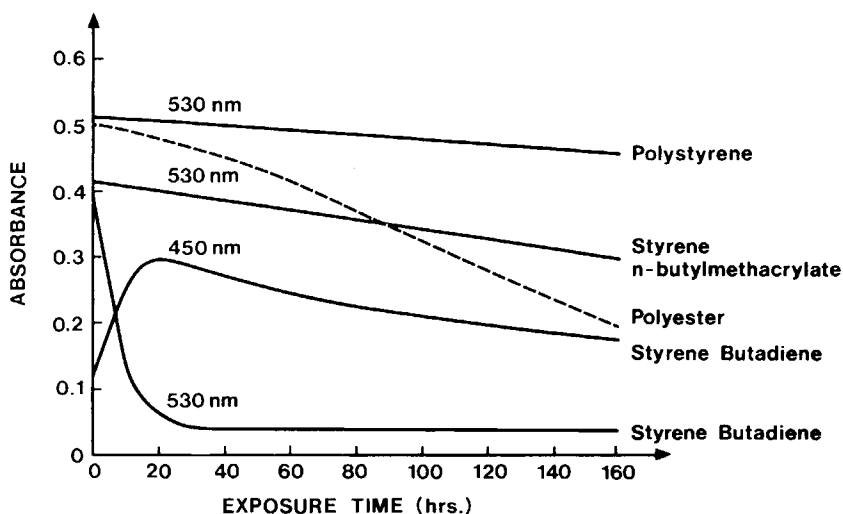


Fig. 8. Absorbance vs. time behavior from fading of red dye **Ia** in several resins at 63°C.

has much greater end-group absorbance above 300 nm than does the virgin polymer. Infrared spectroscopic evidence was also obtained for peroxides ( $3450\text{ cm}^{-1}$ ) and additional carbonyl groups ( $1725\text{ cm}^{-1}$ ) in the faded samples.

In styrene *n*-butylmethacrylate copolymer at 63°C in air, only minor fading was observed, about 30 times slower than in styrene butadiene. Even less fading was observed in polystyrene of comparable  $T_g = 55^\circ\text{C}$ . Some of the spectral information is considered in Figure 8, where the absorbance versus time behavior from several experiments at 63°C is presented for 530 and 450 nm. The increase and subsequent decay of the 450 nm absorbance indicates that the secondary fading of the sulfoxide was slower than the primary red to yellow conversion. That this is more evident at 63°C than at 25° (compare Figs. 4 and 5) indicates that the first process was more temperature sensitive than the second. Temperature dependence studies showed the primary photo-oxidation rate doubles every 10°, while the secondary fading of the sulfoxide is almost the same at 25° and 65°C.

The kinetics of the primary decay were first order in dye concentration: within experimental error, the same half-life was obtained in films of 6–13  $\mu\text{m}$  thickness, at dye loadings of 3–9 weight percent. Table II summarizes the half-life data for the red dye **Ia** in the various resins.

TABLE II  
Half-Lives (in hours) of Red Dye **Ia** in Various Resins

Resin	25°C in air	63°C	
		in air	in N <sub>2</sub>
Polystyrene		750	
Styrene <i>n</i> -butylmethacrylate	> 4000	300	> 1500
Polyester		140	> 1500
Styrene butadiene	70	8	> 1500



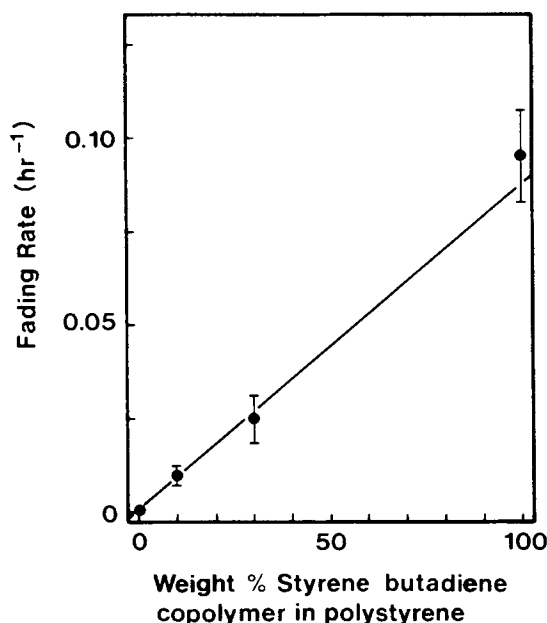


Fig. 9. The effect of double bond concentration on the fading rate of red dye Ia in styrene butadiene/styrene blends at 63°C.

Fading was found to be independent of thioaromatic substituent in structure I with a Hammett rho value near zero within experimental error ( $0.1 \pm 0.2$ ; data not shown). The complete series of these dyes covered a Hammett sigma range from  $-0.27$  for **Ib** to  $0.78$  for **Ih**, yet the half lives were approximately the same:  $18 \text{ h} \pm 40\%$  with no trend.

The main reason for the accelerated photofading in styrene butadiene copolymer compared with other toner resins appears to be the presence of isolated C=C double bonds. Although there are double bonds in the fumarate groups in polyester, the presence of the adjacent carbonyl groups renders them much less sensitive to oxidation, consistent with the observed fading rate styrene butadiene copolymer  $\gg$  polyester  $>$  styrene *n*-butylmethacrylate copolymer.

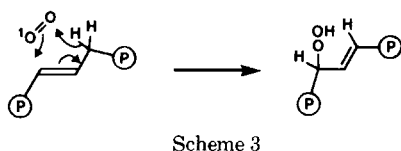
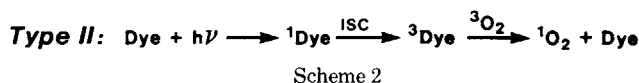
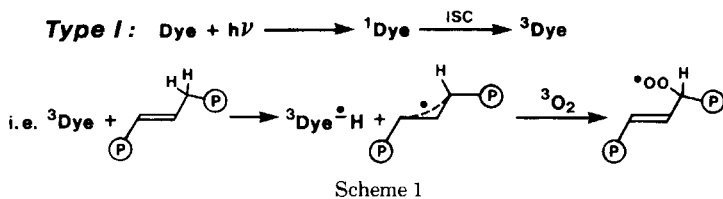
The role of double bonds was quantitatively investigated in a series of experiments where styrene butadiene copolymer was blended with polystyrene to give an overall butadiene content of 0-12% by weight. The fading data in these blended resins is summarized in Figure 9: there is a linear increase in the fading rate at 63° from the very low value for polystyrene to pure styrene butadiene copolymer of 12% butadiene.

### Fading Mechanism

From these observations, the fading rate of the red dye emerges as represented by Eq. (1):

$$\text{rate of fading} = k[\text{dye}][\text{O}_2][\text{C}=\text{C}] + k'[\text{dye}][\text{O}_2] \quad (1)$$

where the second term is relatively minor in the presence of double bonds (Fig. 9). There are two separate, well-recognized phenomena: dye-sensitized photo-

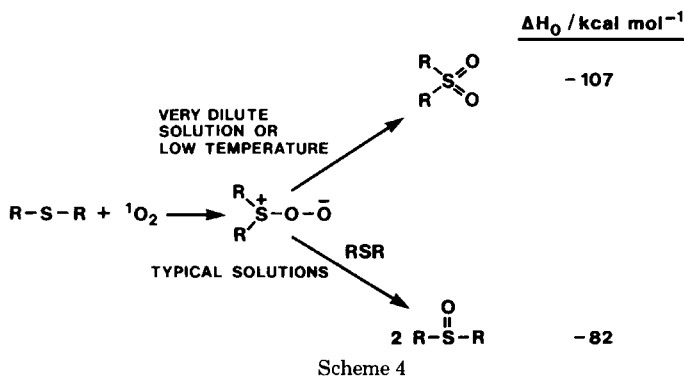


oxidation of the polymer,<sup>3</sup> and photooxidation of the dye itself<sup>2</sup> (i.e., bleaching or fading), and these will be discussed in turn.

**Polymer Photooxidation.** The first of these, dye-sensitized photooxidation of double-bond-containing polymers, is a well known process<sup>5,6</sup> with many parallels to sensitized solution phase photooxidation of olefins.<sup>7,8</sup> There are two types of mechanisms for such photooxidations—the radical Type I (Scheme 1) and singlet oxygen Type II (Scheme 2).<sup>8</sup> Peroxide radicals generated in Type I processes usually lead to auto oxidation and extensive polymer cleavage by a chain mechanism. Singlet oxygen formed by a Type II oxidation is a very reactive species which may oxidize double bonds, sulfides, amines, etc.<sup>8</sup> Singlet oxygen oxidation of double bonds usually produces peroxides by the “ene reaction”<sup>7,8</sup> (Scheme 3). By themselves, these ene-produced peroxides are believed *not* to lead to polymer scission (for example, microwave discharge generated <sup>1</sup>O<sub>2</sub> does not cleave chains<sup>5,6</sup>).

Dye-sensitized photooxidation of butadiene-containing polymers is believed to involve both Type I and II processes, with the radical chain auto oxidation Type I process responsible for the chain scission in solid films.<sup>5-7</sup>

**Dye Bleaching.** With respect to the second phenomenon—photooxidation of the dye—the reaction of <sup>1</sup>O<sub>2</sub> with sulfides is complex, and not well

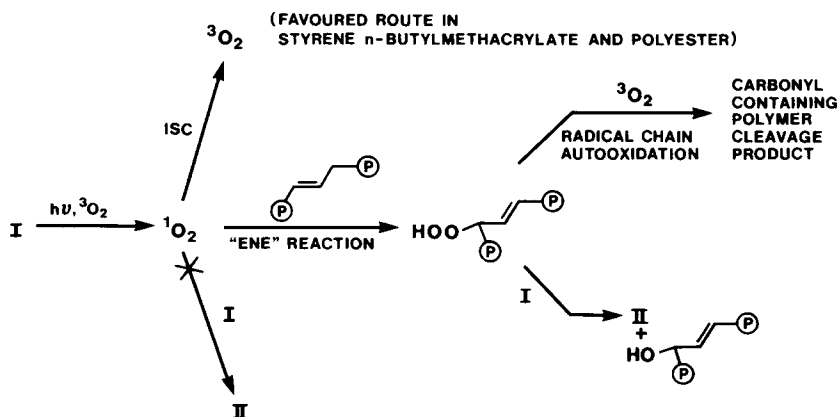


understood.<sup>9-11</sup> Generally, in spite of the apparently less favorable thermodynamics, two sulfoxide molecules are often kinetically obtained in preference to sulfone (Scheme 4). Both diphenyl sulfide and mono- or disubstituted olefins are relatively unreactive to singlet oxygen, compared to alkyl sulfides or tri- and tetrasubstituted olefins.<sup>5,7,9</sup>

From Monroe's olefin studies,<sup>7</sup> one can estimate a second-order rate constant of  $9 \times 10^4$  L/mol s<sup>-1</sup> for attack of singlet oxygen on an isolated, disubstituted double bond, as in styrene butadiene copolymer (see Appendix). With more difficulty, the corresponding rate constant for attack on the red anthraquinone dye **Ia** can be estimated from Monroe's diphenyl sulfide and thioanisole data<sup>9</sup> as  $3 \times 10^4$  L/mol s<sup>-1</sup>. From the 12% butadiene content in styrene butadiene copolymer and a 3% dye loading, the relative concentration ratio [C=C]/[dye] is about 36, and therefore, any <sup>1</sup>O<sub>2</sub> formed in the polymer film would be about 100 times more likely to react with polymer than with dye (relative concentration ratio times relative rate ratio). This factor could be attenuated somewhat by the birth of singlet oxygen preferentially closer to the sensitizing dye molecule than to any particular double bond. Chain scission (defined as  $\bar{M}_{no}/\bar{M}_{nt} - 1$ )<sup>6</sup> was 3 after 19 h of exposure (Fig. 6), a time which corresponds to almost complete decay of the red dye. Given  $\bar{M}_n = 16,000$  at time zero, there was an average of 37 double bonds per chain (1.0 dye molecules per chain), so the rate of scission was 3 to 4 times larger than the rate of bleaching.

This analysis suggests that *the primary fate of the singlet oxygen produced in styrene butadiene copolymer films is polymer oxidation, with the rate of chain scission greater than the rate of fading.* That fading and chain scission are different processes is consistent with earlier work showing no correlation between the photostability of five anthraquinone dyes and their ability to generate singlet oxygen.<sup>4</sup>

Direct reaction between singlet oxygen and dye can easily be ruled out in styrene butadiene copolymer films on several grounds. First, the fading rate ought to be independent of resin, possibly even slower in styrene butadiene copolymer because of competing reaction with double bonds. Second, the kinetics ought to be second order in dye and would require very much higher diffusion constants than is reasonable for solid films. Finally, the fading rate



would be expected to show a strong substituent effect: for example, oxidation of a series of thioanisoles gave a Hammett rho value of  $-1.7$  (Ref. 9)—a far larger effect than we observed (*vide supra*).

However, it is likely that the polymeric peroxides are responsible for oxidation of sulfides to sulfoxide in the dye. Both hydrogen peroxide and alkyl hydroperoxide are known to oxidize sulfur,<sup>12,13</sup> and the mechanism is believed nucleophilic (Hammett rho value of  $-0.98$  for hydrogen peroxide oxidation of diphenyl sulfide in aqueous ethanol<sup>14</sup>). Our rho value near zero in the nonpolar polymer matrix is more consistent with a radical mechanism. Regardless of the precise mechanism of the dye bleaching step, the peroxides are the likely agents, and the overall mechanism can be summarized in Scheme 5.

### Stabilization Against Oxidation

Having determined a basic mechanism for anthraquinone dye fading in styrene butadiene copolymer films, our attention turned to methods to stabilize the polymer against photodegradation, and in so doing, stabilize the colored resins against fading by this mechanism. There are several generic approaches to stabilization which act at different points in Scheme 5 (Refs. 8, 15):

1. Prevent the formation of  $^1\text{O}_2$  with competing absorbers or with quenchers for the excited singlet or triplet states of the dye.
2. Destroy  $^1\text{O}_2$  itself with appropriate quenchers or chemical agents.
3. Destroy the peroxides.
4. Break the radical chain auto oxidation with radical traps.

Ultraviolet absorbers are expected to fail here because the degradation is caused by visible light. Of course, competing visible absorbers cannot be employed as they would change the color. Heller and Blattmann<sup>15</sup> have calculated that, because of limited diffusion in polymer films, quenching of excited singlet or triplet states is unlikely: singlet states are too short-lived and triplets require close contact distances. Possibly  $^1\text{O}_2$  can be quenched in films because it is very much more mobile and longer lived than any excited sensitizer.

Hydroperoxides may be destroyed by a variety of agents, including phosphite or phosphate esters<sup>16</sup> and various metal chelates.<sup>8,17</sup> Figure 10 shows that even 3 weight % (to resin) *tris*(nonylphenyl)phosphite had no effect on the fading rate of red dye I in styrene butadiene copolymer. Metal chelates have the advantage of stabilizing in several modes: quenching  $^1\text{O}_2$  (in solution, at least), decomposing peroxides, and scavenging radicals.<sup>8</sup> Their disadvantage to colored resin applications lies in the fact that they are brown or black in color. Nitroxyls and hindered amines or phenols also stabilize polyolefins by reacting with hydroperoxides and trapping out radicals in auto oxidation chains.<sup>18,19</sup>

$\alpha$ -Tocopherol, the most active chain breaking phenolic antioxidant known,<sup>20</sup> also scavenges  $^1\text{O}_2$  (in solution) by a combination of chemical reaction and quenching, deactivating some 120  $^1\text{O}_2$  before being destroyed.<sup>21</sup> In our red styrene butadiene copolymer films, however, even as much as 3%  $\alpha$ -tocopherol only increased the fading half-life by  $50 \pm 30\%$ .

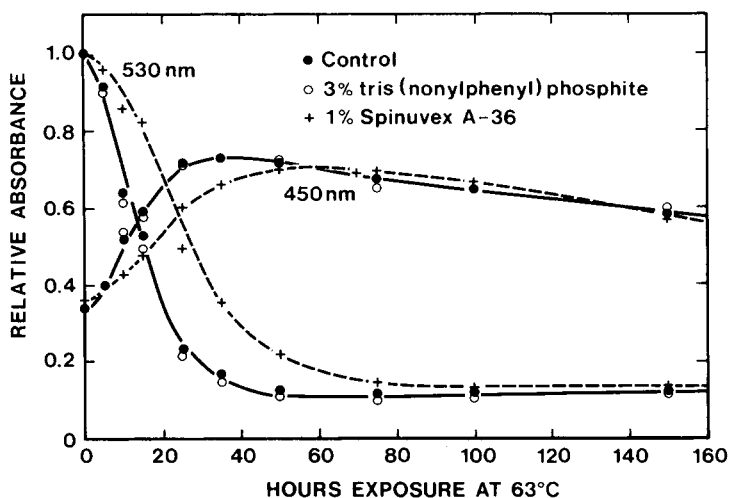


Fig. 10. Fading of red dye Ia in styrene butadiene copolymer film at 63°C with and without stabilizers.

Tinuvin 770 (*bis*(2,2,6,6-tetramethyl-4-piperidiny)sebacate) at 0.25% concentration, is reported to strongly inhibit anthraquinone photosensitized degradation of butadiene polymers by forming nitroxyl radicals which preferentially react with alkyl radicals to form hydroxylamines.<sup>19</sup> In the same class, Spinuvex A-36 (a low molecular weight polymeric piperidino hindered amine stabilizer available from Borg Warner Chemicals Inc, West Virginia), approximately doubles our fading half-life at a 1% loading (Fig. 10). Again, stabilization was still rather poor when compared to the 10 to 100 times accelerative effect of styrene butadiene copolymer vs other polymers.

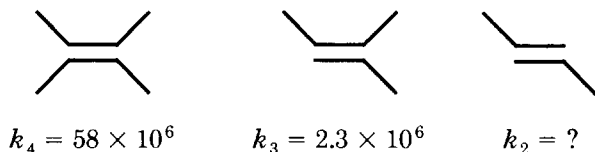
## CONCLUSION

The mechanism of accelerated photofading of red anthraquinone dye Ia in styrene butadiene resins has been investigated. This dye fades up to  $100 \times$  faster in styrene butadiene copolymer than in polystyrene, styrene *n*-butylmethacrylate copolymer, and polyester resins. The primary fading product was identified as the yellow sulfoxide dye IIa, which itself also fades with continued exposure. Concurrent with dye fading, styrene butadiene copolymer resin is extensively degraded by photosensitized oxidation, first from peroxide formation by singlet oxygen in the "ene reaction", and then by radical chain auto oxidation. It is probably the peroxides, rather than singlet oxygen, which attacks the sulfide linkage in thioether anthraquinones. The polyperoxide formation/dye oxidation mechanism appears general for other yellow, blue and red anthraquinone dyes, with readily oxidizable amino, hydroxy, or ethylene groups, and is reflected in the apparently universal fading rate order: styrene butadiene  $\gg$  polyester  $>$  styrene *n*-butylmethacrylate. There is very limited scope for stabilization with classical antioxidants, so oxidizable anthraquinone dyes in styrene butadiene toners are unsuitable for applications requiring high photostability. This unsuitability has been demonstrated to have more to do with the resin (more specifically the double bonds in the

styrene butadiene copolymer) than with the dye, which, in the absence of double bonds, can be remarkably photostable.

### APPENDIX: ESTIMATION OF RATE CONSTANTS FOR SINGLET OXYGEN ATTACK ON POLYMER AND DYE

The double bonds in styrene butadiene may be modeled by 2-butene and rate constants for singlet oxygen attack on polymer and dye estimated as follows (data from Ref. 7):



$$k_2 \sim \frac{k_3}{\text{methyl effect}} = \frac{k_3}{k_4/k_3} = 0.9 \times 10^5 \text{ L/mol s}^{-1}$$

Red dye **1a** can be treated as a substituted diphenyl sulfide ( $k_{\text{PhSPH}} = 8 \times 10^4 \text{ L/mol s}^{-1}$  (Ref. 9)) with substituents *m*-(*i*-Bu), *p*-OH, *m*-CO, and *o*-C=O ( $\Sigma\sigma = -0.17 - 0.37 + 0.38 + 0.50 = 0.32$ ). Using  $\rho = -1.7$  for thioanisoles,<sup>9</sup> the substituted red dye of  $\Sigma\sigma = 0.32$  should react  $3 \times$  slower than  $\text{Ph}_2\text{S}$ , or with  $k \sim 3 \times 10^4 \text{ L/mol s}^{-1}$  if the substituent effects were additive.

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