Photoregulated Sorption Dyes to Polymers. II. Adsorption of Acid Yellow 38 to Hydrophilic Polymers and Its Light-Induced Desorption

K. PETRAK*, L. LEYSHON, and P. DOUGLAS, *Kodak Limited, Research Division, Headstone Drive, Harrow, Middlesex, United Kingdom*

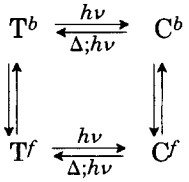
Synopsis

Adsorption of Acid Yellow 38 to, and its light-induced desorption from, various coated polymer layers in water have been studied. Diffusion studies were used to determine the degree of competitive binding between the dye and polymers. It was found that the extent of both adsorption and desorption were different for polymer mixtures as compared to single polymer films. The presence of gelatin crosslinked within the polymer layer increased the amount of dye desorbed upon irradiation.

INTRODUCTION

In the first part of this communication[1] we described the photochemical and thermal isomerization of a water-soluble bis-azo dye, Acid Yellow 38, in aqueous solutions with and without polymers. In this part we will discuss the interaction of the dye with coated polymer films, in particular its light-induced desorption.

When an azo dye is isomerized from the energetically more stable trans to the cis form, a dipole moment across the azo bond is induced and hydrophobicity decreases.[2] Further, the conformation of the dye changes considerably on isomerization. It can be expected that the extent of adsorption of the isomers of the same dye onto a polymer film will be different. In consequence, the adsorption of dye to a polymer may change reversibly on irradiation. Negishi and co-workers[3] showed this using styrene–divinylbenzene copolymer as substrate. Two consecutive processes will thus determine the outcome of the photoinduced desorption: (a) photoisomerization of the dye and (b) the consequent change in the binding equilibria of the isomers. We can consider these in terms of the following equilibria:



Scheme I

* Author for correspondence. Present Address: Advanced Drug Delivery Unit, Ciba-Geigy Pharmaceuticals, Wimblehurst Road, Horsham, West Sussex, United Kingdom.

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where T and C refer to the trans and cis isomers, respectively, and superscripts b and f refer to the dye in the adsorbed and free state, respectively. Any of these equilibria, alone or in combination, can control the dye behavior. In Part I we considered isomerization equilibria; here we will examine those of adsorption and desorption.

EXPERIMENTAL

Materials

Acid Yellow 38 (C.I. 25135) [5-(4-ethoxyphenolazo)-2-(4-(4'-ethoxyphenylazo)-2-sulphophenylthio)benzene sulfonic acid, disodium salt] (obtained from Aldrich Chemical Co., Inc.) was purified using the general method of Robinson and Mills.[4]

The following *polymers* have been used: gelatin, poly(2-vinylpyridine), poly(1-vinylimidazole), poly(1-vinyl-2-methylimidazole), poly(4-vinylpyridine), polyvinylpyrrolidone, poly(1-vinylimidazole)$_9$-co-(1-vinyl-3-hydroxyethylimidazolium chloride)$_1$ (QPVI), poly(1-vinylimidazole)$_8$-co-(1-vinyl-3-benzylimidazolium chloride)$_2$-co-(styrene)$_{10}$ (QPVI-S). The coatings of polymers were prepared as follows: Most polymers were dissolved in water to give a 4 wt % solution, and this solution was mixed with an equal quantity of 4% aqueous gelatin to provide the coating melt. After the addition of surfactant Olin 10G (nonylphenoxypolyglycidol) (Olin Chem. Co.) and the appropriate hardener solutions, coatings were made at coverages of 10 mL ft^{-2} on a polyester base. For coatings without gelatin the polymer solution was diluted with water, while gelatin only coatings were similarly made from the stock aqueous gelatin. "Araldite" Diluent DY022 (bis epoxide) and formaldehyde were used as crosslinking agents (cf. Table I).

Poly(4-vinylpyridine) and poly(2-vinylpyridine) were not directly soluble in water and were dissolved in the minimum quantity of dilute HCl needed to produce a clear solution. The styrene/quaternised vinylimidazole copolymer was insoluble in water, and was coated in the form of an emulsion.

Turbidities of aqueous solutions were determined using a Pye Unicam SP1700 spectrophotometer. The solutions were prepared by mixing the appropriate amounts of the polymer and dye stock solutions at 38°C, and their optical density was measured at 600 nm where neither the dye nor any of the polymers absorb light. The pH values of the aqueous solutions were determined using a PTI-55 pH meter equipped with a glass pH electrode and a temperature compensating probe.

Methods

Measurement of Light-Induced Desorption

The experimental arrangement is shown schematically in Figure 1. It consists of a flow-through adsorption cell (1), peristaltic pump (2), spectrophotometer with a flow cell (3), reservoir (4), tubing (5), light source (6), light filter (7), and recorder (8). A polymer coating (9) was placed in the cell (1), the flow system filled with distilled water, and the appropriate

TABLE I
Light-Initiated Desorption of AY38 from Various Polymers[a]

		R_{AD}	R_D	R_D/R_{AD}
Group 1	Gelatin	No adsorption		
	Poly(2-vinylpyridine) + gelatin[b]			
	Polyvinylpyrrolidone + gelatin[b]			
Group 2	Poly(1-vinylimidazole)[b]	2.43	No desorption	
	QPVI[b]	4.17		
	Poly(1-vinyl-2-methylimidazole)[b]	7.00		
	QPVI-S + gelatin[c]	0.28		
Group 3	Poly(4-vinylpyridine) + gelatin[d]	0.89	10.11	11.36
	Poly(4-vinylpyridine) + gelatin[e]	2.85	7.33	2.57
	Poly(1-vinylimidazole) + gelatin[b]	1.13	2.85	2.52
	QPVI + gelatin[b]	1.04	2.23	2.14
	QPVI + gelatin[c]	1.56	4.26	2.73
	Poly(1-vinyl-2-methylimidazole) + gelatin[b]	1.44	3.55	2.47

[a] At least three determinations were carried out in each case.
[b] Araldite DY022 (Ciba-Geigy) bis-epoxy crosslinker.
[c] Formaldehyde crosslinker.
[d] Poly(4-vinylpyridine)/gelatin 1:1 (by weight); 200 mg ft^{-2} of each polymer; 0.25 wt % of crosslinker (formaldehyde/bis-epoxide = 1:1 by weight) per total polymer weight.
[e] Poly(4-vinylpyridine)/gelatin 1:1 (by weight); 50 mg ft^{-2} of each polymer; 2.5 wt % of crosslinker (bis-epoxide) per total weight of polymer.

amount of all-trans dye solution was added to the reservoir (4) in the dark. Under a constant flow ($\sim$ 8 mL min^{-1}), a decrease in absorbance of the solution with time is a measure of the rate and the extent of adsorption of dye to polymer (cf. Fig. 2). When a near-equilibrium state of adsorption was reached, the film [and through the film also the solution (10)] was exposed to light of the appropriate wavelength through a transparent window in the cell (1). Any changes in absorbance following irradiation were recorded

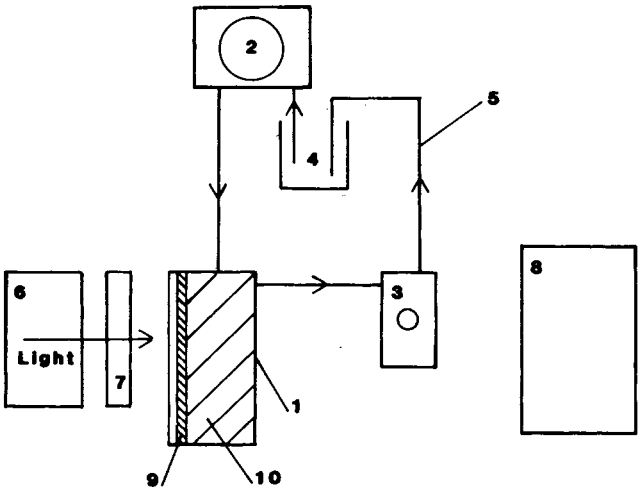

Fig. 1. Schematic representation of the experimental arrangement: (1) adsorption cell; (2) peristaltic pump; (3) spectrophotometer flow cell; (4) reservoir; (5) tubing; (6) light source; (7) light filter; (8) recorder, (9) polymer coating; (10) dye solution.

(Fig. 2). The experiment was continued until a new equilibrium was established.

The light source was a 100-W high-pressure mercury arc, and the collimated beam was filtered through a Balzers 18 filter (nominal transmission wavelength 366 nm, half-bandwidth 11 nm). The area of the coated disk exposed to the dye solution was about 26 cm^2. The total amount of the coated polymer was 6 or 12 mg per disk. The total volume of the circulating solution was kept at 50 mL with the initial dye concentration being 9×10^{-5} mol dm^{-3}.

In our experiments, the light passed through the polymer film before it reached the dye solution. As different polymers will adsorb different amounts of dye, the intensity and spectral distribution of the light reaching the solution will differ from experiment to experiment. Furthermore, the degree of isomerization of the dye on the film will also alter the character of the light incident on the solution. Although this may affect the precise photochemical equilibrium attained in solution, the effect will be small; in all cases irradiation gave a predominantly cis isomeric mixture in the solution phase.

The observed adsorption/desorption behavior of the dye was quantified in terms of the difference between the binding equilibria of the dye to the polymers before and after irradiation. Such equilibria can be expressed simply as the ratio R of the amount of dye in solution ("free" dye) and the amount of dye adsorbed to polymer ("bound" dye):

$$R = c^f/c^b \tag{1}$$

where c^f is the amount of "free" dye in solution at the given equilibrium and c^b is the amount of dye bound to polymer. From the spectroscopic data,

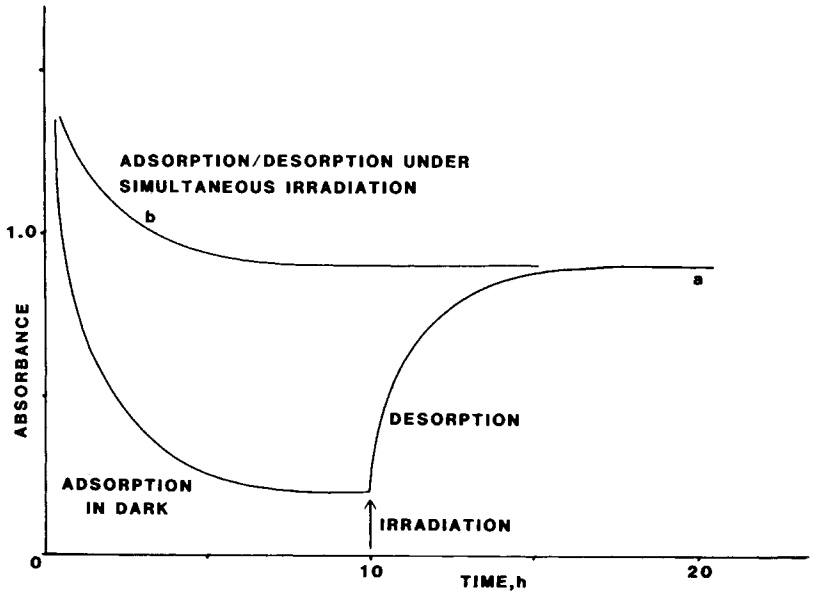

Fig. 2. Adsorption/desorption behavior of AY38.

c^f can be expressed, for unit pathlength, as

$$c^f = A^f/a_\lambda^f \tag{2}$$

and

$$R = A_\lambda^f/(a_\lambda^f \cdot \bar{c} - A_\lambda^f) \tag{3}$$

where $\bar{c}$ is the total concentration of the dye originally in solution, A_λ^f is the absorbance of "free" dye in solution at wavelength λ, and a_λ^f is the molar absorptivity of the dye at wavelength λ. The changes in the absorbance of the dye solution during the adsorption/desorption experiments were measured at 320 nm (an isosbestic point). At an isosbestic point both isomers have the same molar absorptivity so that changes in absorbance are due only to a change in the total concentration of dye in solution.

The *transport* of AY38 was investigated using an experimental arrangement which has been described elsewhere.[5] The increase in the transmittance with time at wavelength $\lambda = 420$ nm in the downstream compartment of the cell was measured using the Brinkman Dipping Probe Colorimeter Model PC/600D equipped with a 2 cm stainless steel probe tip. The upstream compartment of the cell was filled with 20 cm^3 of 9.1×10^{-4} M aqueous solution of the dye. The effective nominal area of the membrane was 6 cm^2. The diffusion cell was housed in an electrically heated aluminium block, and the temperature of the solutions within the cell was maintained at 45 $\pm$ 0.5°C during the steady-state part of the measurement. Both compartments of the cell were stirred using magnetic stirrer bars at about 400 rev min^{-1}. A pure cellulose membrane filter (Schleicher and Schull, RC51; nominal pore size < 0.005 μm) was used as a membrane. The filter was washed in deionized water before each measurement; in between the measurements the membrane was kept in a 50 vol % ethanol/water solution.

RESULTS AND DISCUSSION

We examined a number of polymers to see the effect of the polymer chemical composition on the sorption equilibria. The results are summarized in Table I where the parameters R_{AD} and R_D denote the equilibrium after adsorption in the dark and after photoinduced desorption, respectively. The ratio of R_D/R_{AD} decreases and approaches unity as the amount of desorbed dye decreases.

It can be seen that the polymers fall into three groups: (1) polymer coatings that do not adsorb the dye (e.g., gelatin); (2) polymer coatings that adsorb the dye but the dye does not desorb on irradiation (interestingly, all the polymers coated without gelatin in these experiments fall into this category); (3) polymer coatings that adsorb the dye and then lose some of the dye on irradiation (all the adsorbing polymers coated in a mixture with gelatin, with the single exception of quaternized 1-vinylimidazole/styrene copolymer, belong to this group. Group 1 is of no interest to us. For Group 2 the photoisomerization appears to be irrelevant, at least over the time scale of our experiment, in which the distinction between very slow de-

sorption rates and equilibria heavily displaced towards the adsorbed dye is not possible. The mixture of polymers (group 3) exhibit behaviour that seems to involve all four equilibria (Scheme 1). Figure 2 shows that a true equilibrium is reached since the degree of adsorption is the same no matter whether adsorption preceeds or is concomitant with irradition.

In a recent report[6] an examination was made of the interactions that take place in a mixture of two polymers and a solute using methyl organe as adsorbate. Briefly, the extent of binding between a polymer and a solute can be estimated from the effect of polymer in solution on the rate of diffusion of the solute through a membrane. For a unit membrane area, the flux F across the membrane is given by the expression $F = -D(dc/dx) = D \cdot \Delta C/l$. ($D$ is the diffusion coefficient for the dye through the membrane, l is the membrane thickness, and ΔC is the difference in the solute concentration on the two sides of the membrane). If F is the flux of the dye in the absence of any polymer and F^1 is the flux in the presence of an interacting polymer then $F/F^1 = \Delta C/\Delta C^1$. (We assume that D and l remain constant). From the ratio of fluxes we obtain an estimate of the concentration of the free dye in solution in the presence of polymer, and since the total concentration of the solute is known, the amount of solute "bound" to the polymer can be calculated.

In a ternary mixture of a dye and two polymers, the dye molecules can interact with just one or with both polymers, and in addition the two polymers can interact with each other. If only one of the polymers interacts with the dye, the dye will be in competition with the other polymer for the "binding sites" on the adsorbing polymer. As a result of the interference by the second polymer with the binding of the dye, less dye is adsorbed; consequently, the concentration of the "free" dye in solution increases, and the flux of the dye across the membrane increases. The ratio of the amount of solute bound to one polymer to the amount of solute bound to a mixture of two polymers is then a measure of interaction between the two polymers. We measured the rate of diffusion of AY38 dye through a pure cellulose membrane in the presence of gelatin, QPVI, and in mixtures of the two polymers. The results are given in Table II. It can be seen that, within the concentration range employed, QPVI adsorbed at least 97% of the available dye as compared to the maximum of 24% for gelatin. The effect of added gelatin is clearly shown by the increase in flux of the dye; however, the

TABLE II
The Effect of Polymers on the Diffusion of AY38 through Cellulose Membrane

Polymer 1	Polymer 1 concn (wt %)	Polymer 2	Polymer 2 concn (wt %)	Flux $\times 10^8$ mol cm^{-2} min^{-1}	Free dye concn $\times 10^4$ mol dm^{-3}
—	—	—	—	5.70	9.1
QPVI	0.61	—	—	0.00	0.0
QPVI	0.61	Gelatin	0.61	0.11	0.18
QPVI	0.06	—	—	0.15	0.24
QPVI	0.06	Gelatin	0.06	0.94	1.5
Gelatin	0.61	—	—	4.30	6.9
Gelatin	0.06	—	—	4.70	7.5

amount of free dye is still relatively small. At a 1:1 ratio of QPVI to gelatin, depending on the overall polymer concentration, up to 13% of AY38 could be prevented from binding to QPVI. The effect of gelatin on the flux of AY38 is thus similar to that observed previously[6] for methyl orange.

Although the adsorption experiments showed almost no adsorption of AY38 to gelatin, the diffusion experiment clearly indicated that the dye does bind to gelatin to a small degree. [The ratio of gelatin to dye was, however, about two times higher in the latter experiment (at 0.06 wt.% of gelatin).] We conclude that gelatin interacts with QPVI in such a way that it either reduces the number of, or weakens the dye interactions with, the "binding sites" on QPVI.

In seeming contradiction to this conclusion is our observation that the amount of AY38 taken up by coated QPVI is actually increased by the presence of gelatin. The size of this increase is too large to be attributed to the adsorption of the dye by gelatin (cf. Table I). As we see it, in coatings of QPVI alone, dye is strongly bound near the surface of the film, and there is a barrier to the subsequent access of dye into the bulk of the coating. The presence in the mixture of a hydrophilic polymer that does not bind the dye (e.g., gelatin) makes it possible for the dye to penetrate the entire volume of the polymer layer, thus making use of more "binding" sites. Microscopic examination of crosssections of dyed coatings supports this interpretation; in QPVI alone dye was concentrated at the surface but a more uniform distribution was apparent in the QPVI/gelatin coating.

In Part I, we showed that isomerization of the dye does occur in the presence of this polymer in solution, and the turbidity measurements suggest a change in dye–polymer binding upon isomerization (Fig. 3). However,

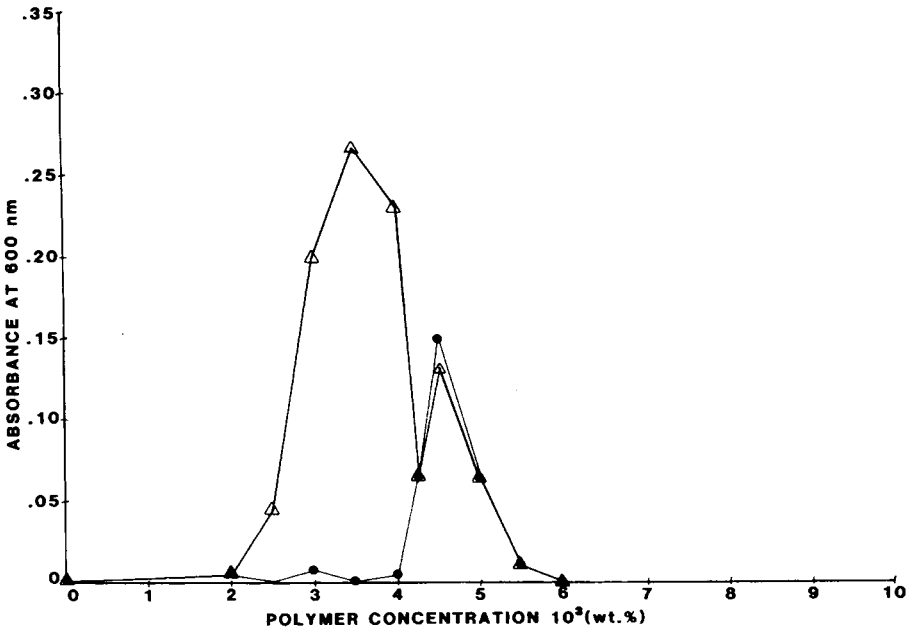

Fig. 3. The effect of polymer concentration on the turbidity of QPVI/AY38 aqueous solutions: (△) upon irradiation; (●) in dark. Dye concentration: $3.6 \times 10^{-5}M$.

there was no desorption of the dye from a film of QPVI alone (cf. Table 1), even though significant isomerization of the dye was observed in the solution in contact with the polymer layer. We can conclude that either both cis and trans isomers are strongly adsorbed, or that the lack of desorption results from kinetic barriers and true equilibria are not reached. The desorption of the dye from mixed polymer films upon irradiation shows that the binding equilibrium for the cis isomer is shifted, relative to that of trans, in favor of the dye in solution. This is a similar situation to that described by Negishi et al.[3] for AY38 and a styrene/divinylbenzene copolymer. From thermodynamic measurements they argued that the light-induced desorption was caused by a decrease in the hydrophobic interactions between dye and polymer.

Our results show that a shift in the binding equilibria can be brought about by the presence of a second, competing polymer. In these circumstances binding may still predominantly involve only one polymer, although formation of a polymer/polymer complex having different binding properties cannot be discounted.

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