

Photoregulated Sorption of Dyes to Polymers I. The Effect of Polymers on Some Photochemical Properties of Acid Yellow 38

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Synopsis

The effect of polymers [gelatin, dextran, poly(vinyl alcohol), polyvinylimidazoles] on the photochemical and thermal isomerization of the water-soluble bisazo dye, Acid Yellow 38, has been studied. The absorption spectrum curve of the cis AY38 isomer was obtained using the method of Fischer. We have shown that the rate of thermal cis-trans isomerization of AY38 is first order and independent of pH from 6 to 9. An activation energy of $84 \pm 4 \text{ kJ mol}^{-1}$ has been calculated for this process. The effect of added polymers on the rate of this conversion is relatively small. The quantum yields for the trans-cis and cis-trans conversions have been estimated to be 0.15 ± 0.01 and 0.34 ± 0.03 , respectively, for irradiation at 380 nm. Only polyvinylimidazoles were found to influence the behavior of the dye to any degree. For quaternized polyvinylimidazole the polymer/dye ratio determined solution turbidity, wavelength of maximum absorption, molar absorptivity, and the degree of conversion at photoequilibrium. The effect of polymer was interpreted in terms of increased dye/dye interactions due to high local concentration of the dye bound to polymer. The charge neutralization and crosslinking by the dye due to ionic interactions are seen to be the cause of polymer/dye complex precipitation. Precipitation occurs over a narrow [polymer]/[dye] ratio range.

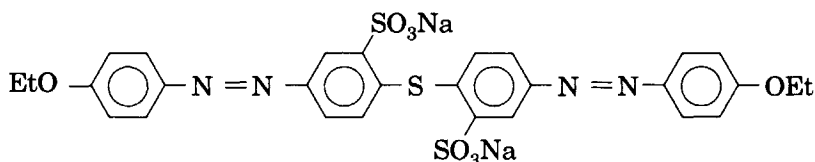
INTRODUCTION

The response of polymers to light has become a worthwhile area of study since the behavior of such polymers may be used for photoregulation of various polymer properties. Our work was inspired by the results of Ishihara and co-workers^{1,2} on the photoinduced wettability and binding ability of azoaromatic polymers. Their work in turn follows an earlier research by Lovrien³ on the photoregulation of polymer conformation in solution by means of photochromic ligands.

In this communication we examine the adsorption of Acid Yellow 38 (AY38) to, and its light-induced desorption from, various hydrophilic polymers and their mixtures. In the first part we report our results on the pertinent photochemistry of AY38 in aqueous solutions, including the influence of dissolved polymers on the relevant isomerization processes. In the second part we examine the effect of polymer composition on the outcome of adsorption and the light-induced desorption.

Acid Yellow 38 [5-(4-ethoxyphenylazo)-2-(4-(4'-ethoxyphenylazo)-2-sulphenylthio)benzene sulfonic acid, disodium salt], is a symmetrical bisazo dye, isomerization of which is possible at both azo ($-\text{N}=\text{N}-$) bonds. Three

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geometric isomers can be envisaged, i.e., trans-trans, trans-cis, and cis-cis. AY38 has been used in earlier isomerization studies,⁴ but its photochemical behavior has not been fully described in the published literature.

EXPERIMENTAL

Acid Yellow 38 (C.I.25135), obtained from Aldrich Chem. Co., was purified using the general method of Robinson and Mills.⁵ Dextran (Sigma Chem. Co., $M_n = 5.0 \times 10^5$ Dalton), gelatin (Eastman Kodak Co., $M_w = 2.1 \times 10^5$ Dalton) and poly(vinyl alcohol) (PVA) (Elvanol 7130, DuPont Co. Ltd., $M_n = 7.6 \times 10^4$ Dalton) were used as received. Poly(1-vinylimidazole) (PVI) was prepared by aqueous radical polymerization of the monomer and purified by aqueous ultrafiltration ($M_w = 1.8 \times 10^4$ Dalton). Poly(1-vinyl-3-hydroxyethylimidazolium chloride)₁-co-(1-vinylimidazole)₉ (QPVI) was prepared by reacting poly(1-vinylimidazole) with 2-chloroethanol, and purified by ultrafiltration (cut-off 5×10^3 Dalton). The extent of quaternization was determined by titrating the halide counterion with silver nitrate. The number-average molecular weight of the polymer was 4.5×10^3 Dalton ($M_w = 1.9 \times 10^4$ Dalton). The molecular weight of gelatin was estimated viscometrically; the molecular weights (as polyethylene glycol equivalents) of all the other polymers were determined by aqueous gel-permeation chromatography. The NMR spectra were observed in FT mode with a JEOL FX100 instrument fitted with a 5 mm dual probe (¹H/¹³C). Deuterium internal lock was established on the solvent signal.

The electronic spectra were recorded using a Pye Unicam SP1700 or a Perkin-Elmer Lambda 5 spectrophotometer. Solutions were irradiated with light from a 100 W high pressure mercury arc passed through a Bausch and Lomb high intensity grating monochromator. The solutions were not stirred during irradiation, but shaken between measurements. Cells of 1 cm path length (~3 mL volume) were used throughout.

The irradiation intensities were determined using both a calibrated Hilger-Schwartz thermopile and the chemical actinometry method described by Heller and Langen.⁶ The two methods agreed to within 5%. The flux of photons from the source at the boundary of the irradiated system was 7.6×10^{14} photons $s^{-1} cm^{-2}$ at 360 nm and 9.2×10^{14} photons $s^{-1} cm^{-2}$ at 380 nm, for a 20 nm bandpass. The absorption spectrum of pure cis AY38 was determined indirectly by the method of Fischer,⁷ which requires irradiation to photoequilibrium by light of different wavelengths. In these experiments the solution was irradiated by light from the excitation source of a Perkin-Elmer MPF-44E spectrofluorimeter (5 nm bandpass). In order for the dye to be initially in its trans-trans form, the solutions were kept at 60°C overnight prior to use.

The turbidity of aqueous solutions containing the given amount of polymer and the dye were determined using a Pye Unicam SP1700 spectro-

photometer. The solutions were prepared by mixing the appropriate amounts of the polymer and dye stock solutions at 30°C, and their optical density was measured at 600 nm, at which wavelength both dye and polymer are transparent.

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.

Polymer concentrations are usually expressed as wt %. For some results with QPVI the polymer concentration is expressed in molar terms with respect to monomer units in order to facilitate comparison between the polymer and dye concentrations. Since the average molecular weight of the monomer unit in QPVI is about 102, the molar concentration of monomer units is approximately wt %/10.

RESULTS AND DISCUSSION

The photoinduced *trans-cis* isomerization of azo compounds was demonstrated by Hartley.⁸ In general, the *trans* isomer of an azo compound is more stable than the *cis* species.⁹ Our samples at room temperature contained not less than 99.8 mol % of the *trans-trans* isomer, as determined by NMR (see below). The UV-visible electronic spectrum of a solution of all-*trans* AY38 in water is shown in Figure 1(a). From this curve we calculate the molar absorptivity of *trans-trans* AY38 at 377 nm to be $4.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. This compares with a value of $4.22 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ reported by Negishi et al.⁴ On exposure to light of a suitable wavelength AY38 dye isomerizes to give eventually a photostationary mixture, the composition of which depends on the wavelength of the irradiating light and the ambient temperature. The progress of such an isomerization can be followed spectrophotometrically as illustrated by curves b-e of Figure 1.

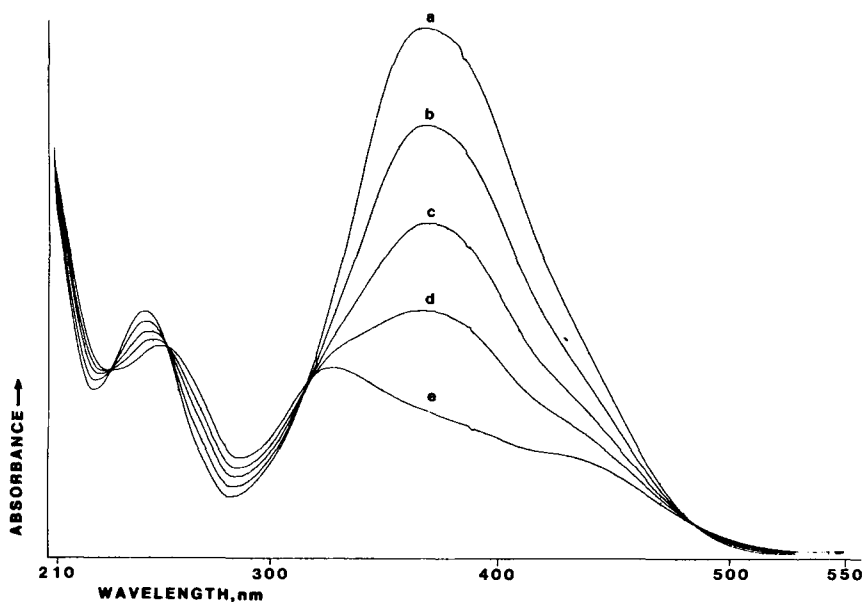


Fig. 1. Light-induced isomerization of AY38: (a) all-*trans* AY38; (b-e) *trans-cis* mixtures; 380 nm irradiation, 20 nm bandpass.

Curve e is the absorption spectrum of the photostationary mixture under the conditions of the particular experiment, and curves b–d represent intermediate mixtures in order of increasing irradiation time. The isomerization is fully thermally reversible, i.e., the original curve a is restored on warming the solution in the dark. The existence of four well-defined isosbestic points at 234, 260, 320, and 488 nm suggests that only two species participate in the isomerisation but this interpretation was refuted by NMR spectroscopy. Figure 2 shows part of the NMR trace obtained after photoisomerization of a concentrated (about $1 \times 10^{-2}M$) solution of AY38 in D_2O . Before irradiation the signals labelled b, c, and d were absent but the signal, a, was very prominent. From tables of chemical shifts and coupling information (Published by Sadtler, Philadelphia–London–Heyden, 1982) (Sadtler Handbook of Proton NMR Spectra) this signal was assigned to the aromatic proton ortho to the sulphonate group in an all-trans configured molecule. The new signal, d, appearing after photoisomerisation was likewise assigned to the same ortho proton in an all-cis configuration, while the equal intensity peaks b and c were consistent with the predicted positions of the ortho proton signals arising respectively from trans and cis configurations in a mixed trans–cis isomer. Thus the NMR evidence clearly indicates the presence of three distinct species in the photoisomerized mixture, viz, trans–trans, trans–cis, and cis–cis AY38. To rationalize this apparent contradiction, we conclude that the electronic transitions associated with one azo bond in the AY38 molecule are not significantly changed by the configuration of the other azo group. Hence trans–cis AY38 is spectrophotometrically indistinguishable from a mixture of all-trans and all-cis

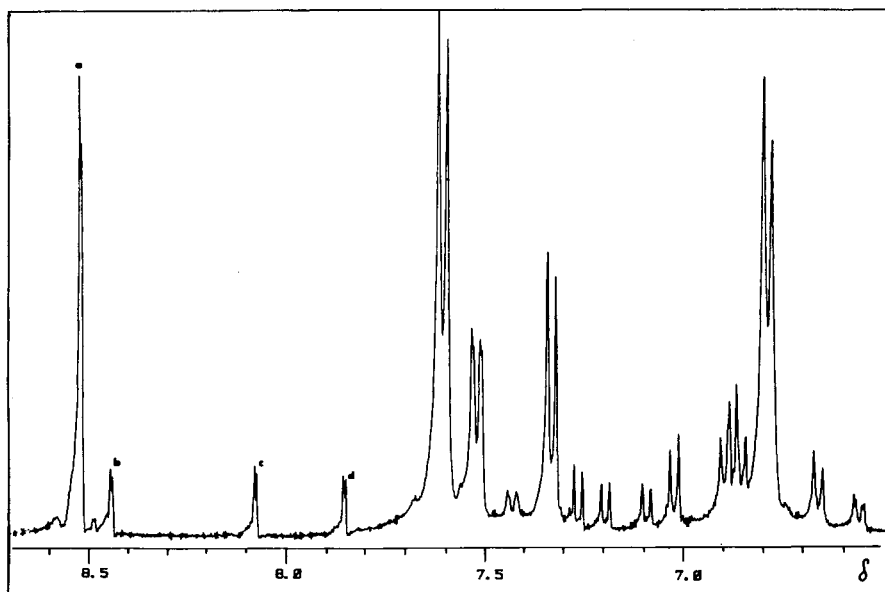


Fig. 2. 1H -NMR spectrum of a mixture of trans and cis isomers of AY38. Labeled peaks are for the aromatic proton adjacent to the sulfonate group: (a) all-trans; (b) trans from trans–cis; (c) cis from trans–cis; (d) all-cis.

AY38, and it is acceptable to quantify the amount of trans and cis dye in a mixture without specifying the exact configuration of each molecule.

While spectroscopic data for pure trans AY38 are available, we could find no published information concerning the cis isomer. Because the absorption bands of the two isomers overlap (cf. Fig. 1), it is not possible to produce pure cis AY38 photochemically and we have, therefore, used the indirect method of Fischer⁷ to calculate its absorption spectrum. The following experimental data were required: (i) the absorption spectrum of an aqueous solution of pure trans AY38; (ii) the absorption spectra after photoequilibration by light of two different wavelengths. Inherent in the method are the assumptions that the rate of any thermal isomerization is small relative to the photochemical processes and that the ratios of the quantum yields for the photoisomerizations are the same at both irradiating wavelengths. The former assumption is valid since under our conditions at the photostationary state, the ratio of the photochemical to thermal cis-trans isomerization rates is ca. 100. We believe that the latter assumption is also valid since the spectra calculated from any pair of photostationary states reached using 330, 360, and 390 nm irradiations were very similar (calculated absorption maxima were at identical wavelengths and the absorptivities were within 2%). The curve we obtained is shown in Figure 3, with $\alpha_{\max} = 1.9 \times 10^4$, 1.5×10^4 , and $5.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\max} = 260$, 323, and 444 nm, respectively.

Quantum Yield of Light-Induced Isomerization of AY38 Dye

The quantum yield of a photochemical process (Φ) is defined as $\Phi = n/q$, where n is the number of molecules converted and q is the number of quanta of light absorbed. This expression may be rewritten as

$$\Phi = - \frac{dc/dt}{E}$$

where $(-dc/dt)$ is the rate of change of concentration of reactant ($\text{mol dm}^{-3} \text{ s}^{-1}$) and E is the rate of absorption of energy ($\text{einstein dm}^{-3} \text{ s}^{-1}$). If we confine ourselves to measurements of initial rates of change, using solutions containing initially only the trans-trans isomer, we can eliminate complications due to the reverse isomerization. Our calculated value of quantum yield for the trans to cis conversion is 0.15 ± 0.01 for 380 nm irradiation, 20 nm bandpass (an average of three experiments, initial absorbance 1.5 at 380 nm). The true quantum yield may be somewhat higher since the solutions were not stirred. The known value of the quantum yield of trans to cis isomerization, in conjunction with a knowledge of the isomeric composition of the photoequilibrium mixture, and hence the relative absorbance due to each isomer, allow us to calculate the quantum yield of the photoinduced reverse cis-trans isomerization since at photoequilibrium the rates of both isomerizations are equal, i.e.,

$$\frac{\Phi_{\text{trans-cis}}}{\Phi_{\text{cis-trans}}} = \frac{A_{\text{cis}}}{A_{\text{trans}}} = \frac{\alpha_{\text{cis}}[\text{AY38}]_{\text{cis}}}{\alpha_{\text{trans}}[\text{AY38}]_{\text{trans}}}$$

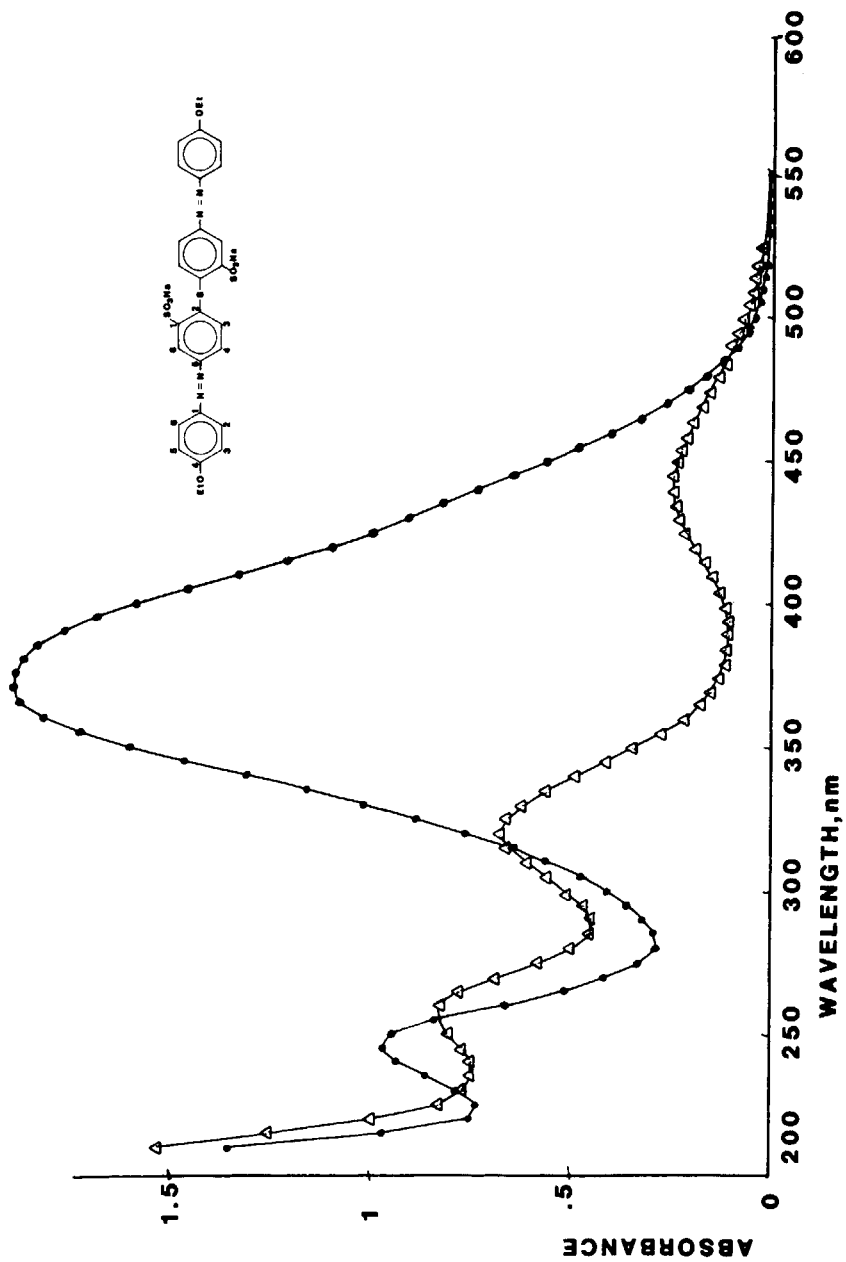


Fig. 3. Electronic spectra of AY38 isomers: (●) measured all-trans; (△) calculated all-cis. Dye concentration $4.3 \times 10^{-5} M$.

where A_{cis} and A_{trans} are the values of absorbance in the equilibrium mixture due to the cis and trans isomers, respectively. Using this relationship, we calculate $\Phi_{cis-trans} = 0.34 \pm 0.03$ assuming that the two azo-groups in any one molecule isomerize independently.

Thermal Cis-Trans Isomerization

The trans AY38 isomer is more stable than its cis counterpart, and there is a thermally activated conversion of cis to trans. Starting from the predominantly (~ 80 mol %) cis photostationary mixture obtained by irradiation at 380 nm, the thermal back reaction followed first-order kinetics over 3 half-lives (for example, at 52°C, the correlation coefficient of the data vs. time plot, $R = -0.99995$). This shows that any cis azo bond in AY38 thermally isomerizes at the same rate irrespective of the conformation of the rest of the molecule. From the temperature dependence of the thermal isomerization rate (cf. Table I), an activation energy of 84 ± 4 kJ mol⁻¹ was determined for this process. This appears to be a typical value for azo compounds.⁹

Effect of Dissolved Polymers on the Isomerization of AY38

In Part II of this communication we discuss the light-induced desorption of AY38 from various polymer films. To aid the understanding of the results presented in Part II we studied the effect of dissolved polymers on the photoisomerization of trans AY38 in aqueous solution and on the thermal reversion of the cis isomer. We chose to investigate five different polymers: dextran, gelatin, poly(vinyl alcohol), poly(1-vinylimidazole), and poly(1-vinylimidazole) partially (10 mol %) quaternized with chloroethanol. Each polymer was investigated over a 10-fold concentration span with the exception of the quaternized poly(1-vinylimidazole), which was studied over a much wider range. The initial, light-induced decrease in optical density of AY38 at 380 nm and the photostationary states reached in the presence of the polymers was determined. The results are shown in Table II, and Figure 4 shows some of the isomerization curves. It can be seen from Table II that dextran and PVA have a negligible effect on the behavior of the dye in water. Gelatin exerts a small but measurable effect on the isomerization process, while QPVI and PVI have a profound influence on both the value of the final optical density and the rate at which it is reached. The different behavior of the polymers can be rationalized by variations in

TABLE I
The Effect of Temperature on the Rate of Thermal Cis-Trans Isomerization of AY38 in Water

Temperature (°C)	Rate constant (s ⁻¹ × 10 ⁴)
40	0.52
52	1.5
60	5.1
70	8.2

TABLE II
The Effect of Polymers on the Photochemical Behavior of AY38^a

Polymer	Polymer conc (wt %)	Initial rate of change of absorbance ^b ($s^{-1} \times 10^3$)	% of initial absorbance at photostationary state	[P]/[D] region (as in text)
Dextran	2	4.63	19.9	
	0.2	4.22	26.5	
PVA	2	4.97	22.1	
	0.2	4.83	27.8	
Gelatin	2	3.7	23.7	
	0.2	4.63	26.3	
PVI	2	2.87	34.0	
	0.2	3.2	37.5	
QPVI	2	3.17	30.7	d
	0.2	2.63	45.4	c
	0.02	2.65	54.2	c
	0.02	2.27	56.1	c
	7.5×10^{-3}	2.37	58.4	c
	5.0×10^{-3}	2.27	59.6	b
	4.5×10^{-3}	2.25	58.1	b
	2.5×10^{-3}	1.97	63.1	b
	1.0×10^{-3}	3.94	34.0	b
	7.0×10^{-4}	3.57	33.3	b
	4.0×10^{-4}	4.83	26.7	b
	1.1×10^{-4}	4.67	27.3	a
	3.6×10^{-5}	4.53	29.1	a
None ^c	—	4.88	25.6	

^aAbsorbance measurements made at 380 nm; [AY38] = $3.5 \times 10^{-6} M$ (initial absorbance 1.5); irradiation wavelength 380 nm; bandpass 20 nm;

^b Measured from change in optical density following 1 min irradiation;

^c Average of three determinations.

polymer-dye binding, and the observed changes in photochemistry could result from variations in spectra, quantum yields, and thermal isomerization rates.

It is known that the rate of thermal isomerization is, for many azo compounds, dependent on solvent and pH.^{9,10} Since the polymer solutions used here were of variable pH within the range 6–8, we examined the effect of pH on the ratio of AY38 isomerization.

Within the range used in this work no effect of pH was evident; the rate constant of the thermal cis-trans isomerization varied, over the pH range from 6 to 9, by only $\pm 5\%$ from its average value. The light-induced isomerization shows a similar lack of sensitivity to the changes in the pH of the environment. In the presence of interacting polymers the reaction kinetics of the thermal cis-trans isomerization remain first order, but the rate constant increases slightly, as can be seen from Table III. This increase is not, however, large enough to account for the different photostationary states of AY38/polymer mixtures.

TABLE III
Thermal Cis-Trans Conversion of AY38 in Aqueous Solutions of Polymers^a

Polymer	(wt %)	T (°C)	First order rate constant ($s^{-1} \times 10^4$)
Gelatin	(2)	60	5.91
	(0.2)		5.63
Dextran	(2)	60	6.97
	(0.2)		5.60
PVA	(2)	60	6.55
	(0.2)		5.67
PVI	(2)	60	11.50
	(0.2)		10.83
QPVI	(2)	60	8.35
	(0.2)		9.70

^a pH value of the polymer solutions 6-8.

It should be kept in mind that these rates were measured from photostationary states which inevitably varied from polymer to polymer (cf. Table II). However, thermal isomerization rate constants in the presence of QPVI were the same irrespective of whether polymer was added to a previously photoequilibrated aqueous solution of the dye or whether the dye was photoequilibrated in the presence of polymer, suggesting that using different photostationary states as starting points in measuring the above rates is not an important factor. Both the position of the absorption maximum (at

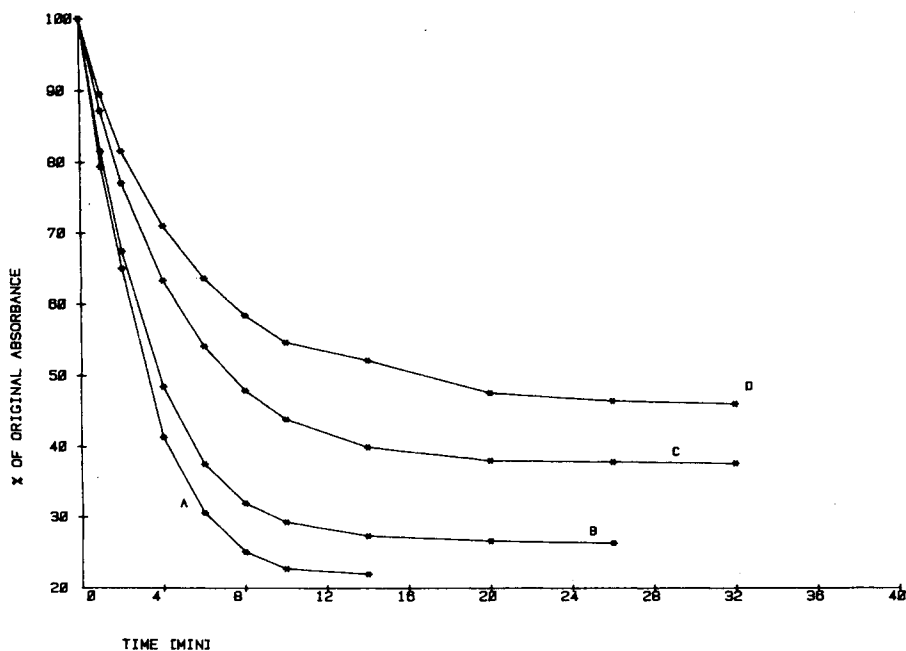


Fig. 4. Isomerization of AY38 in the presence of polymers in aqueous solutions: (A) no polymer; (B) gelatin; (C) PVI; (D) QPVI. Polymer concentration 0.2 wt %; irradiation at 380 nm, 20 nm bandpass; monitoring wavelength 380 nm; initial absorbance 1.5.

about 380 nm) and the turbidity of the solutions were found to vary as a function of QPVI concentration (cf. Figs. 5 and 6). (In a less extensive study, a similar dependence of turbidity and wavelength of maximum absorption on $[P]/[D]$ was found using a dye concentration of $3.3 \times 10^{-6} M$.) Based on this and the effect of polymer on the final optical densities of the irradiated solutions (cf. Table II) we propose to discuss the polymer/dye interactions in terms of four regions defined, for our particular case of QPVI and AY38, as having the following polymer/dye ratios: (a) $[P]/[D] < 1$, (b) $1 < [P]/[D] < 20$, (c) $20 < [P]/[D] < 6000$, and (d) $[P]/[D] > 6000$. Region a is characterized by no change in the position of the absorption maximum or the photostationary state compared to dye alone in water.

At higher polymer concentrations (region b) the absorption band moved progressively to its maximum wavelength ($[P]/[D] \sim 7$); the polymer/dye complex remained soluble. Increasing polymer concentration further to $[P]/[D] \sim 10$ caused the solution to become turbid, and it remained turbid until the $[P]/[D]$ ratio exceeded 17. Above this value clear solutions were obtained. Since we could not detect any precipitation with the uncharged version of the polymer, i.e., PVI, we consider the ionic interactions to be crucial for turbidity, and that neutralization of charges on the polymer by the dye, coupled with the possibility of crosslinking by the difunctional dye, play a major role. These processes are most likely to be significant in the region where the ratio of the positive to negative charges is from 0.5 to 1.

Bearing in mind that only about 10% of the monomer units in the polymer are quaternized, this corresponds to $[P]/[D]$ ratios from 10 to 20. Assuming an even distribution of the positive charges on the polymer chain, the large

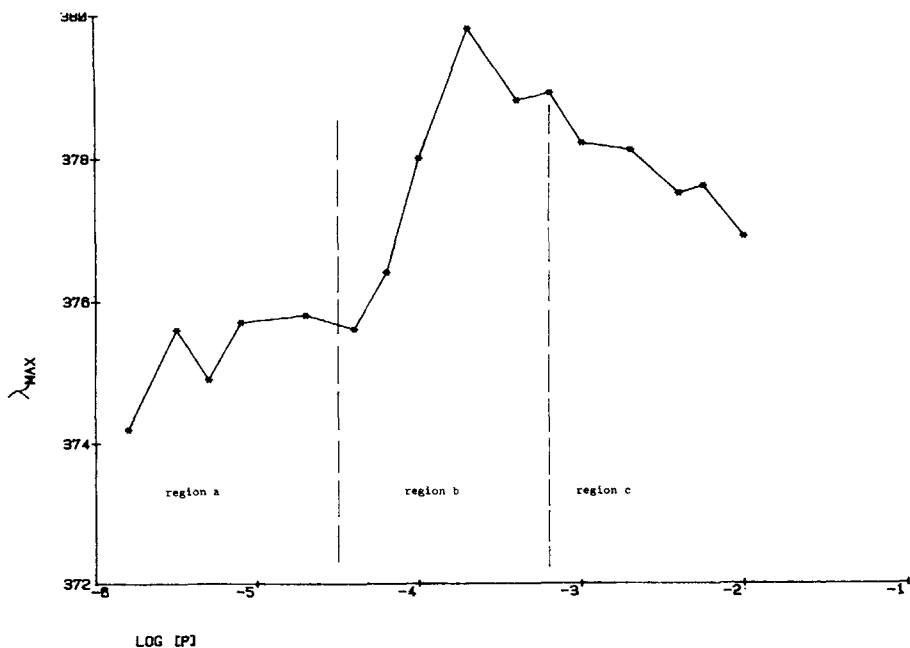


Fig. 5. Position of absorption maximum (λ_{max}) of AY38 as a function of QPVI concentration, $[P]$, expressed as molar concentration of monomer units. Dye concentration $3.3 \times 10^{-5} M$.

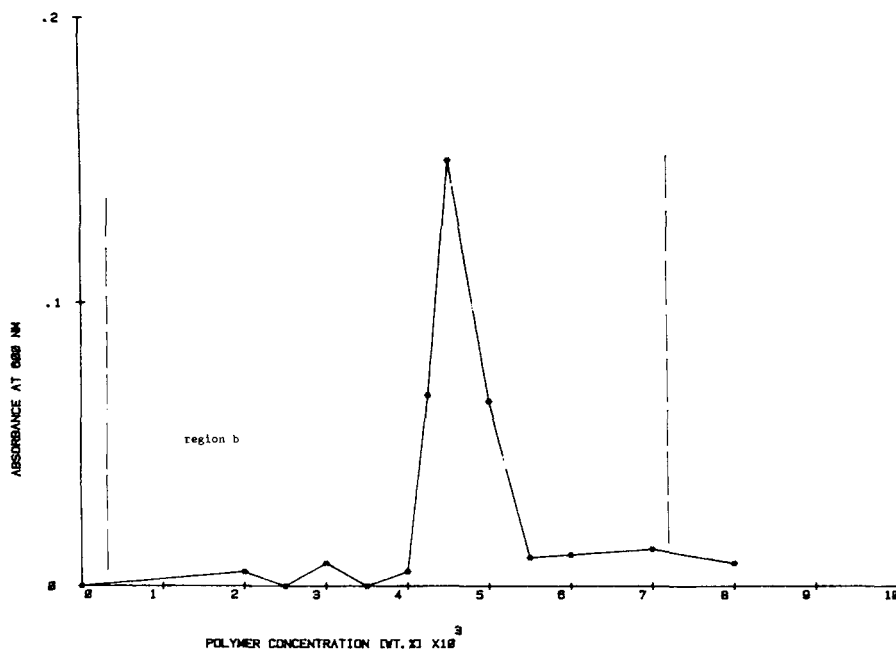


Fig. 6. Solution turbidity as a function of QPVI concentration. Dye concentration $3.6 \times 10^{-5} M$.

distance between the charges will make it unlikely that a dye molecule will interact ionically with the adjacent quaternary sites. Under such conditions, the crosslinking of the polymer chains by the dye is a likely contributing factor to turbidity. At charge ratios < 0.5 it is likely that any one dye molecule will interact with just one quaternary site, leaving pendent anions to solubilize the polymer/dye complex. At charge ratios higher than 1 (i.e., for $[P]/[D] > 20$) (regions c and d) the excess of polymer keeps the polymer/dye complex soluble. Since over region b the turbidity of the solution changes on irradiation (cf. Part II), it would not be prudent to draw a definite conclusion from the measurements of the photostationary state in this range.

The region c is again typified by absence of turbidity and by a slow decrease in the position of λ_{max} with increasing polymer concentration. The final optical densities obtained on irradiation (Table II) are also a function of polymer concentration, decreasing as the polymer concentration increases. This trend continues until region d is reached at which point these properties of the dye approximate to those seen in aqueous solution of AY38 alone.

The apparent decrease in the conversion of trans dye to its cis isomer at $[P]/[D]$ immediately past the turbid region could be due to changes in the spectra of both trans and cis isomers or changes in the relative quantum yields of isomerization. Although the molar absorptivity of trans isomer decreases in this $[P]/[D]$ region by about 15% relative to its value in water, this is not large enough to account for the apparent changes in the photostationary state.

In order to examine the possible changes in the spectrum of the cis isomer in the presence of polymer at these concentrations, aliquots of concentrated polymer solution were added to a dye solution of known trans/cis (43% trans, 57% cis) ratio. The minor spectral changes observed were consistent with the previously observed polymer-induced changes in the trans isomer spectrum. We can conclude that in this spectral region (300–500 nm) there are no major polymer-induced changes occurring in the cis spectrum. We have shown already that the effect of thermal back isomerization is negligible, and believe that the changes in photostationary states are due to changes in dye photochemistry upon binding. From our binding experiments (cf. Part II) we know that about 97% of the dye is bound to QPVI at $[P]/[D]$ about 7, but we cannot invoke the existence of specific binding of the dye to the polymer as a cause of the change in photochemical behavior since at high polymer concentrations photostationary states approach those seen in the absence of polymer.

It would appear that there is a fraction of the dye which photoisomerizes with a very low quantum yield; the proportion of this component is at a maximum in the turbidity region and decreases as the amount of polymer in the mixture increases. From our measurements, at a $[P]/[D]$ of 20, about 30% of the trans isomer will not undergo isomerization even after 8 h of irradiation. The apparent drop in the initial isomerization rate across the regions b, c, and d is partly due to this fraction of dye molecules absorbing a significant portion of the incident light. Along with this "inner filter" effect, changes in the microviscosity of the dye environment may contribute to a decrease in the quantum yield of isomerization. This behavior is well known for azo dyes covalently bound to polymer.¹¹ The maximum effect on the trans–cis photoisomerization is seen when (a) the majority of the dye is bound and (b) the local concentration of the bound dye is very high. This would suggest that dye/dye interactions are the determining factor in modifying the dye photochemical behavior in our case.

We failed to detect any spectral evidence of aggregation for AY38 in aqueous solution up to $1 \times 10^{-3} M$ concentration, although surface tension measurements gave the cmc for AY38 close to $10^{-3} M$, indicating that there is a tendency for the dye to aggregate at high concentration. We do not suggest, however, that the dye/dye interactions between polymer-bound molecules are necessarily the same as those at high concentration in solution. In this context, in a study of sodium dodecylsulfate (SDS) in association with the non-ionic water-soluble polymers, poly(*N*-vinylpyrrolidone) (PVP) and polyethyleneoxide (PEO), Turro et al.¹² have argued for the formation of premicelles cooperatively associated with the polymers. They assumed that at a high polymer to surfactant ratio there was no significant polymer/surfactant interaction. This contrasts with our interpretation of the results given here where we see the dye as being totally bound above $[P]/[D] \sim 10$, but spatially separated at very high $[P]/[D]$ ratios. Dye/dye interactions are thus prevented. In their experiments with pyrene as fluorescence probe, the probe appears to be sensitive in a fairly specific way to a micellar environment and is therefore unlikely to detect interactions between individual SDS molecules and polymers. However, when they used

11-(3-hexyl-1-indoyl)undecyl sulfate, a fluorescent surfactant probe at high polymer/probe ratios and in the absence of added SDS an interaction between the probe and PVP was clearly indicated by a shift in the emission maximum.

CONCLUSIONS

The absorption spectrum curve of the cis AY38 isomer was obtained using the method of Fischer. We have shown that the rate of thermal cis-trans isomerization of AY38 is 1st order and independent of pH from 6 to 9. An activation energy of $84 \pm 4 \text{ kJ mol}^{-1}$ has been calculated for this process. The effect of added polymers on the rate of this conversion is relatively small.

For QPVI, photostationary states, turbidity, wavelength of maximum absorption, and molar absorptivity were all found to depend on the polymer/dye ratio, and the effect of polymer was interpreted in terms of increased dye/dye interactions due to high local concentration of the dye bound to polymer. The charge neutralization and crosslinking by the dye due to ionic interactions are seen to be the cause of polymer/dye complex precipitation which occurs over a narrow [P]/[D] ratio range.

Our conclusions, although arrived at by different reasoning are reminiscent of the studies on the interactions between organic ions of opposite and unequal charges,¹³ and may be helpful in the understanding of interactions between large polymeric organic materials such as antigen and antibody.¹⁴

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