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Photochromic behaviour of Berry Red studied in solution and polymer films

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Abstract

In this work, the photokinetic study of *Reversacol Berry Red* (2,2-bis(4-methoxyphenyl)-5,6-dimethyl-2H-naphtho[1,2-b]pyran), a photochromic compound from James Robinson Ltd., has been carried out in solution and in polymeric films (Paraloid B-72 and Polyvinyl butyral) in order to quantitatively characterize its photochromic properties by means of objective parameters in different environments.

In solution, *Berry Red* shows reversible and intense photocolouration at room temperature and significant solvatochromic effect in the spectrum of the coloured form. Embedded into polymeric films, *Berry Red* maintains its thermally reversible photochromic behaviour. However, the photocolouration quantum yield is appreciably reduced and the kinetic parameters of bleaching are significantly altered. The matrix has the effect of lowering both the activation energy (up to a half of the value in solution) and the pre-exponential factor of thermal bleaching (by about seven orders of magnitude). These compensating effects make the bleaching rates in films close to that in solution. The negative values of activation entropy determined in polymer films are related to the rearrangement of the molecule into the activated complex structure.

Keywords: Photochromism; Reversacol Berry Red; Photokinetics; Photochromic polymer films

1. Introduction

Photochromic compounds which show perspectives in applications are usually embedded in solid matrices to be easily handled and even easily miniaturized. It is important that technological development of photoactivable systems, such as photochromes, be associated to basic studies aimed at determining their properties, such as the activating wavelength range, response time, and intensity of photocolouration (or colourability) in terms of chemical–physical parameters (wavelengths and molar coefficients of absorption, photochemical quantum yields, rate constants and activation energies of the thermal processes). These properties, preliminarily determined in solution, where the results are more easily obtainable and quantitatively interpretable, have been also determined in polymer films of potential applications. In fact, while the study of photochromes in dilute solutions allows their characterization in the absence of significant effects due to intermolecular interactions, in films, the environment can affect the nature, energy and relaxation dynamics of the excited states, thus changing the time scale of the reactions and also the chromatic properties of the system. Therefore, these molecules can be used either as sensors of external perturbations or as probes of the properties of the surrounding microenvironment.

In this paper, a photokinetic study of *Reversacol Berry Red* (2,2-bis(4-methoxyphenyl)-5,6-dimethyl-2H-naphtho [1,2-b]pyran), Scheme 1, a photochromic compound from James Robinson Ltd., belonging to the class of chromenes [1], is carried out in solution, where *Berry Red* has been reported to show reversible and intense red photocolouration at room temperature [2], and then into two polymeric films (Paraloid B-72 and Polyvinyl Butyral) to determine whether the photochromic properties were maintained and could be characterized by means of photokinetic parameters.

For this molecule a model of its interactions in a poly(methylmethacrilate) matrix, has been developed by others [3] following the variation of the glass transition temperature. Some patents have been produced concerning the photochromic behaviour of *Berry Red* in polymer layer [4] and potential applications in photochromic lenses [5,6]. However, at our best knowledge, no quantitative data concerning photochemistry yields and thermal kinetics have been reported before.

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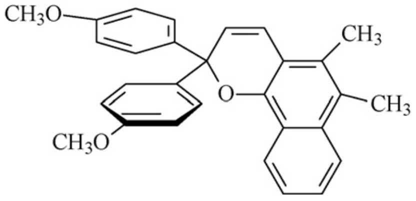


Scheme 1.

2. Materials and methods

2.1. Materials

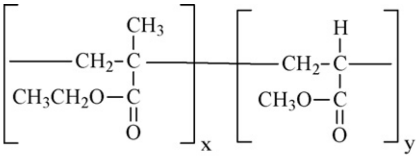
Berry Red was kindly provided by the James Robinson Ltd. Its purity (>98%) was checked by HPLC. The photokinetic measurements were carried out in 3-methylpentane (3MP, BDH) and toluene (Fluka). Other solvents used to investigate solvatochromic properties were acetonitrile (ACN, Fluka), diethylether (DE, Fluka), ethanol (EtOH, Carlo Erba), methanol (MeOH, Fluka) and ethylacetate (EtAc, Fluka). The solvents were purified when necessary.

The polymers used for the film preparations were an acrylic resin, Paraloid B-72 (PB72), which is a 70:30 copolymer of ethyl methacrylate and methyl acrylate, Scheme 2, and a vinylic resin, poly(vinyl butyral), PVB, a copolymer of vinyl butyral (80 wt.%), vinyl alcohol and vinyl acetate, Scheme 3, both purchased from Aldrich.

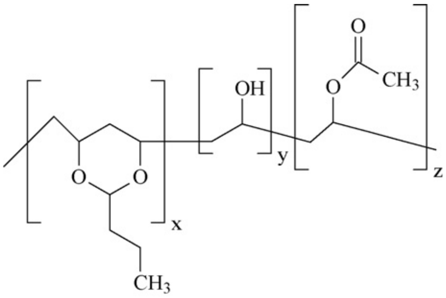
They have different T_g values (40 °C for PB72 [7] and 60 °C for PVB [8] and elastic modulus (150 N mm^{-2} for PB72 [9] and 394 N mm^{-2} for PVB [8]).

2.2. Measurements in solution

The absorption spectra were recorded using a HP 8453 diode-array spectrophotometer. Irradiation of the sample solutions was carried out in a 1 cm cell-path in the spectrophotometer holder, at a right angle to the monitoring beam, using a fibre-optic system. A 125 W Xe lamp, coupled with a Jobin-Yvon H10 UV monochromator, was used for irradiation and an Oxford Instruments cryostat for the temperature control. A grey filter (10% transmittance) was inserted between the sample and the spectrophotometer source, to avoid that a fraction of the UV light intensity might reach the sample, thus inducing photochemistry.



Scheme 2.



Scheme 3.

The quantum yields of the closed to open form photocolouration ($\Phi_{C\rightarrow O}$) and back photobleaching ($\Phi_{O\rightarrow C}$) were spectrophotometrically determined in 3MP and toluene using concentrations in the range 10^{-4} to 10^{-5} mol dm^{-3}. Potassium ferrioxalate actinometry was used to measure the radiation intensity, which was typically on the order of 2–3 × 10^{-7} moles of quanta dm^{-3} s^{-1}. The uncertainty in the quantum yield determinations in solution was about 10%.

The equation [10] used to describe the colour-forming kinetics was:

$$\frac{\mathrm{d}A_O}{\mathrm{d}t} = \varepsilon_O \times \Phi_{C\rightarrow O} I_C - k_\Delta A_O \tag{1}$$

where A_O is the absorbance of the open (coloured) form at the analysis wavelength, I_C is the light intensity absorbed by the closed form at the irradiation wavelength, ε_O is the molar absorption coefficient of the coloured form at the analysis wavelength and k_Δ is the rate constant of the thermal bleaching. Eq. (1) can be rearranged to:

$$\frac{\mathrm{d}A_O}{\mathrm{d}t} = \varepsilon_O \times \Phi_{C\rightarrow O}\varepsilon_{iso} I^0 F A^0 - A_O[I^0 \varepsilon_{iso} \Phi_{C\rightarrow O} + k_\Delta] \tag{2}$$

where ε_{iso} is the molar absorption coefficient at the irradiation wavelength (isosbestic point), F is the photokinetic factor ($F = [1 - \exp(-2.3A')]/A'$, where A' is the total absorbance at the excitation wavelength (λ_{exc}) [10]), I^0 is the intensity of the incident light and A^0 is the initial absorbance at λ_{exc}. The kinetics of the thermal ring-opening reaction were recorded in the dark, following the colour-bleaching of the irradiated solution after switching off the UV source. Arrhenius plots were determined in the 275–310 K temperature range. Filtering of the monitoring light of the spectrophotometer was increased (a 80% transmittance filter was added to that of 10% transmittance) to avoid the induction of the back photochemical reaction. From Eq. (2) and absorbance-time data sets, $\Phi_{C\rightarrow O}$ and ε_O could be evaluated.

The photobleaching quantum yield was determined by irradiating the thermally bleached solution with monochromatic light and following the colour fading up to 30% transformation, based on the rate equation:

$$\frac{-\mathrm{d}A_O}{\mathrm{d}t} = \varepsilon_O \Phi_{C\rightarrow O} I^0 (1 - 10^{-A'_O}) \tag{3}$$

where A'_O is the absorbance of the coloured form at λ_{exc}. Both A_O and A'_O are time dependent variables. Based on Eq. (3), the quantum yield was obtained from the linear plot of $-\mathrm{d}A_O/\mathrm{d}t$ vs. 10^{A_O}, which gives $\varepsilon_O \times \Phi_{O\rightarrow C}$ from both the intercept and slope.

2.3. Measurements in polymer films

For the preparation of the polymer matrix, 0.2 g of the polymer (PB72 or PVB) were added to 5 ml of acetone (5 wt.%) and stirred until completely dissolved. Then, a weighted amount (0.05 wt.%) of Berry Red was added to the polymer and the solution was stirred to mix. Then it was poured over a smooth surface by multiple spreading-drying cycles. The film formed was peeled-off from the surface and stored in the dark. Its thickness was about 100–150 μm.

Photocolouration experiments on the photochromic films were carried out using the same spectrophotometer/irradiating lamp/monochromator set-up as for solutions. For the temperature control a SPECAC variable temperature cell (in the 290–310 K range) with silica fused windows was used. The irradiation was performed with an optic fibre focused on the sample through a mobile mirror. The quantum yields were determined by treating the experimental time/absorbance data according to the initial rate method [10]. The ferrioxalate actinometer (1 cm^3 solution) and the polymer film were positioned using the same geometrical arrangement with respect to the irradiating source. The actinometer response (I^0_{act}) was related to the absorbance (A_{C}) of the photochromic film at λ_{exc} and its thickness (0.012 ± 0.002 cm). Thus the light intensity (I_{C}) absorbed by the sample could be determined from the following relationship, where A_{act} is the absorbance of the actinometer:

$$I_{\mathrm{C}} = A_{\mathrm{C}} \times \frac{I^0_{\mathrm{act}}}{A_{\mathrm{act}}} \quad \text{(absorbed quanta per 0.012 cm}^3\,\text{s}^{-1}\text{)} \qquad (4)$$

Due to various sources of error, such as the imperfect homogeneity of the film over the 1 cm^2 irradiated surface, uncertainty on the thickness of the film and slightly different geometry of the chemical actinometer, the yield values are affected by a consistent error, estimated around ±30%.

For atomic force microscopy (AFM) measurements a Solver PRO (NT-MDT) microscope was used. AFM provides nanometre lateral and sub-angstrom vertical resolution, allowing nanoscale characterization of polymeric materials [11].

3. Results

3.1. Study in solution

The absorption spectrum of Berry Red shows a high energy intense band (λ < 300 nm) and a less intense, structured and extended absorption region at lower energy (310–370 nm), Fig. 1, spectrum 1. In this latter band active vibrational modes are observed of about 1350–1400 cm^{-1}, corresponding to breathing modes of the benzene ring, which were also present in other chromenes [12]. In the present case, however, the peak separation is not regular, that could be due to the overlap of different electronic and/or vibronic transitions. Upon UV irradiation, colouration is observed with appearance of a new absorption band around 500 nm, whereas an increase in absorbance is also observed in the UV region, Fig. 1, spectrum 2.

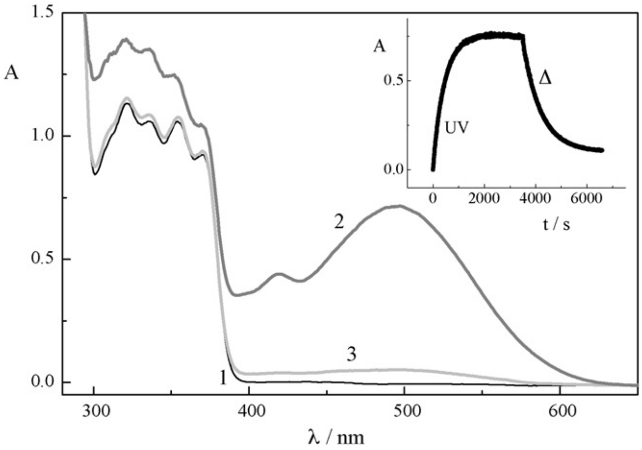


Fig. 1. Spectral evolution of a 2.75 × 10^{-4} mol dm^{-3} toluene solution of Berry Red at 300 K: (1) before UV irradiation; (2) after UV irradiation; (3) after thermal bleaching. Inset: colour forming and colour-bleaching kinetics at 495 nm.

The photochromism of this compound was observed in several solvents of different polarity and hydrogen-bonding capability. A marked positive solvatochromic effect was revealed for the coloured form, which is well described, with the exception for toluene, in terms of the $E_{\mathrm{T}}(30)$ Dimroth parameter [13], Fig. 2, by the relationship:

$$\nu(\mathrm{cm}^{-1}) = 22400 - 48E_{\mathrm{T}}(30) \qquad (5)$$

The red shift observed (from 478 nm in 3MP to 507 nm in EtOH) is in the direction expected for a π, π* transition (Fig. 2).

The kinetic study revealed the formation of two photoisomers. They showed similar spectral patterns in the visible range but different stability: one was thermoreversible and the other photoreversible, Fig. 1, spectrum 3. On the basis of steric considerations and by analogy with other chromenes [14], the thermoreversible isomer is assigned to the transoid-*cis* form and the photoreversible isomer to the transoid-*trans* form. The latter was present in a very low percentage, whatever the operative conditions were. The spectral characteristics of Berry Red coloured and colourless forms in two solvents, 3MP and toluene, are

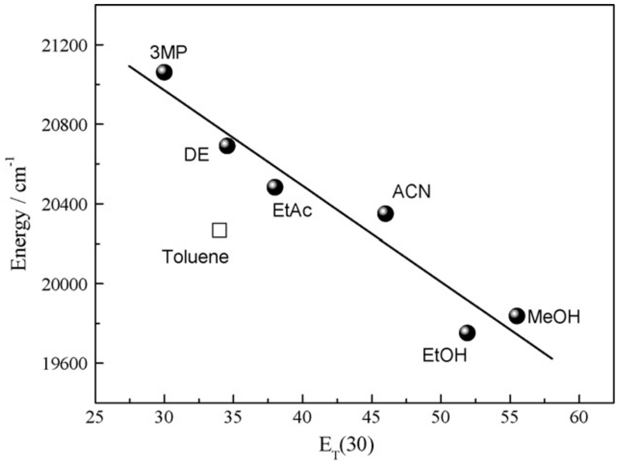


Fig. 2. Correlation diagram for the coloured band of Berry Red with the $E_{\mathrm{T}}(30)$ Dimroth parameter.

Table 1
Spectral characteristics (λ_{max}/nm and molar absorption coefficient, ε_{max}/dm^3 mol^{-1} cm^{-1}) of the closed colourless form and of the open coloured form, photocolouration ($\Phi_{C\rightarrow O}$) and photobleaching ($\Phi_{O\rightarrow C}$) quantum yields for Berry Red in 3-methylpentane and toluene at 220 K

Solvent	Colourless		Coloured		$\Phi_{C\rightarrow O}$	$\Phi_{O\rightarrow C}$
	λ_{max}	ε_{max}	λ_{max}	ε_{max}		
3MP	368, 280	4000, 52,100	484	41,200	0.37	0.0006
Toluene	369	4000	496	37,600	0.41	0.03

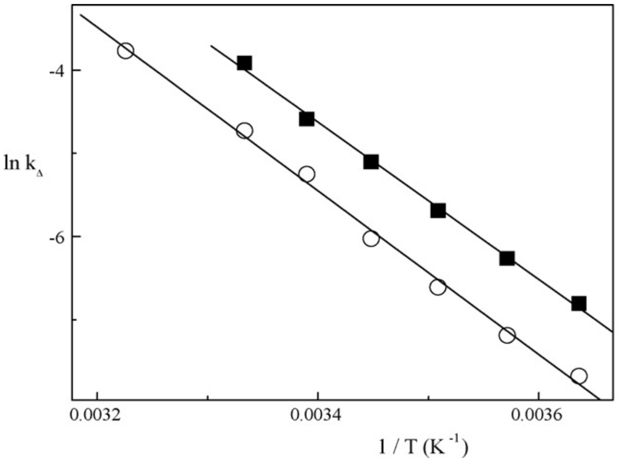


Fig. 3. Arrhenius plots for the thermal bleaching of Berry Red in 3MP (■) and toluene (○).

reported in Table 1, along with the quantum yields of the forward and back photoreactions.

The study of the photocolouration/decolouration reactions as a function of temperature and the data treatment based on Arrhenius plots (Fig. 3) allowed the kinetic parameters of the thermal bleaching to be obtained (Table 2). It can be observed that the thermal reaction is slower in toluene than in 3MP, resulting in a lower colourability in the latter solvent.

Table 2
Kinetic parameters for the decolouration of Berry Red in 3MP and toluene

T (K)	3MP		Toluene	
	k_Δ (s^{-1})	Kinetic parameters	k_Δ (s^{-1})	Kinetic parameters
300	0.0200		0.00890	
295	0.0102	$E_a = 79$ kJ mol^{-1}	0.00530	$E_a = 82$ kJ mol^{-1}
280	0.0019	$k_0 = 9 \times 10^{11}$ s^{-1}	0.00076	$k_0 = 1.4 \times 10^{12}$ s^{-1}
275	0.0011		0.00046	

3.2. *Study in polymer films*

The photochromic behaviour of *Berry Red* was investigated in PB72 and PVB films. In both polymers it could be photocoloured with UV light and thermally bleached in the dark. The thin films obtained were analysed by atomic force microscopy to obtain information about the surface morphology. An example of the images obtained is shown in Fig. 4. From the appearance of the images it can be inferred that the photochromic compound induces a structural self-organization of the matrix. The aggregation is in large part in form of linear strands in PB72 (Fig. 4) and in balls in PVB (not shown here).

The spectrum of the coloured form in PB72 shows a maximum at 498 nm (Fig. 5), corresponding to a solvent of significant polarity ($E_T(30) \sim 49$, by interpolation from the diagram of Fig. 2).

Measurements of UV-photocolouration and thermal bleaching were carried out in the 293–309 K temperature range. In this interval the bleaching rate constant varied from 3×10^{-2} to 8×10^{-3} s^{-1}. The kinetics at temperatures lower than 300 K showed a biexponential trend, while were well fitted with a monoexponential function at higher temperatures.

The activation energy, obtained from the Arrhenius plot (Fig. 6), is 61 kJ mol^{-1} and the frequency factor is 7×10^8 s^{-1}.

The absorption spectrum of *Berry Red* in a PVB film does not show substantial differences from that in PB72. However, the bleaching kinetics are biexponential over the whole temperature range explored (293–313 K), with the two kinetic components, k_1 and k_2, ranging from 1.4×10^{-2} to 4×10^{-3} s^{-1} and from 1.5×10^{-3} to 4×10^{-4} s^{-1}, respectively. The activation energy

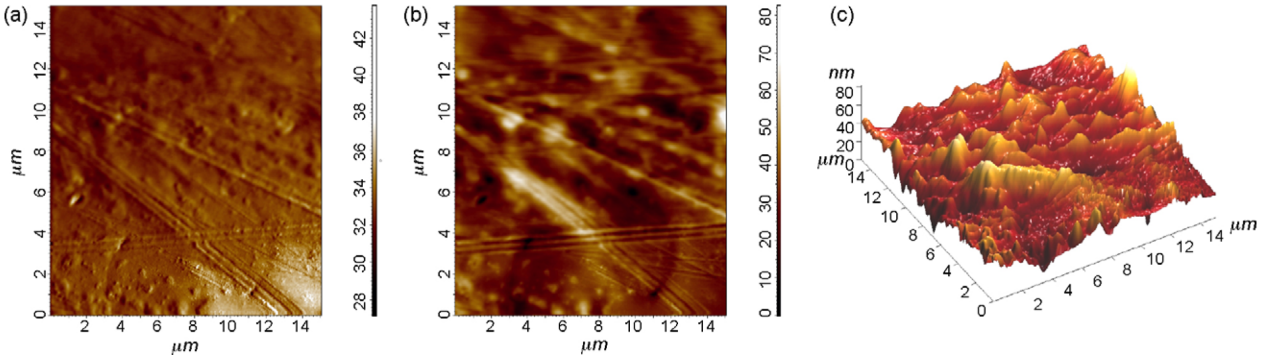


Fig. 4. AFM images of a PB72 film containing Berry Red on mica: (a) Internal sensor image; (b) topographic image; (c) 3D image.

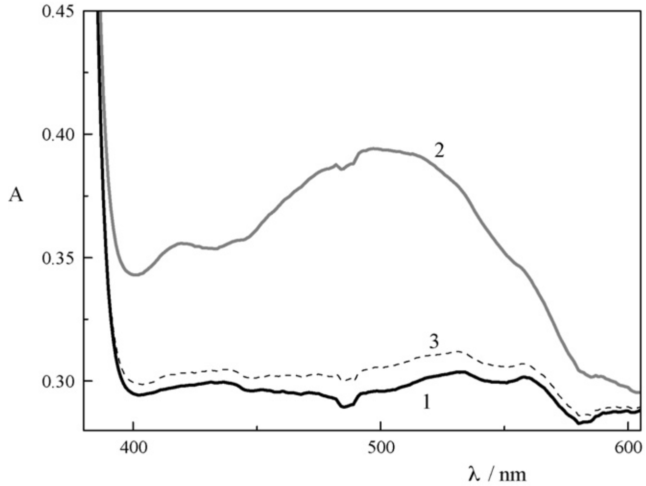


Fig. 5. Spectral evolution of Berry Red in a PB72 film: before irradiation (black), after UV irradiation (grey) and after thermal bleaching (dashed), at 290 K.

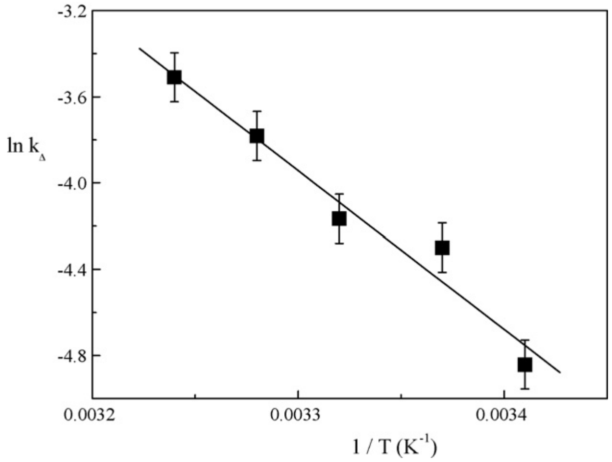


Fig. 6. Arrhenius plot for the thermal bleaching of Berry Red in a PB72 film.

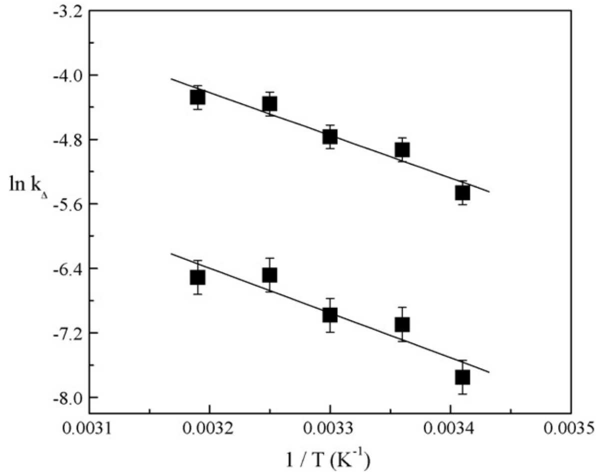


Fig. 7. Arrhenius plots for the thermal bleaching of Berry Red in a PVB polymer film.

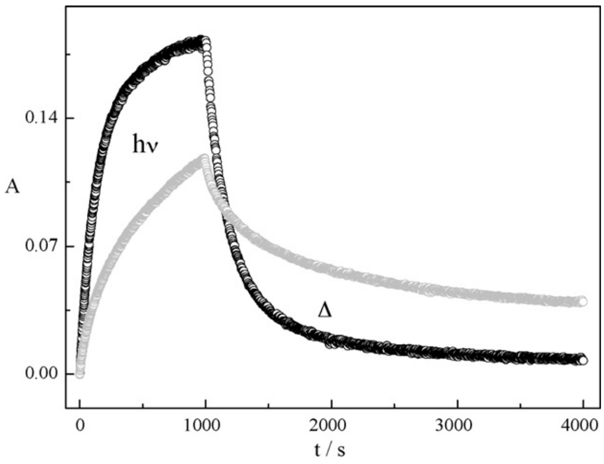


Fig. 8. Photocolouration and thermal bleaching kinetics of Berry Red in a PB72 film (black) and in a PVB film (grey) at 302 K.

Table 3
Kinetic parameters and thermodynamic activation parameters of the thermal bleaching and reaction quantum yields of Berry Red at 300 K in different environments

	Toluene	PB72 film	PVB film	
k_Δ (s^{-1}) (300 K)	0.0089	0.0151	0.0079	0.0008
E_a (kJ mol^{-1})	82	61	44	46
A (s^{-1})	1.4×10^{12}	7×10^{8}	3×10^{5}	9×10^{4}
$\Delta S^{\#}$ (J mol^{-1} K^{-1})	−19	−85	−147	−159
$\Delta H^{\#}$ (kJ mol^{-1})	79.5	58.5	41.5	43.5
$\Delta G^{\#}$ (kJ mol^{-1})	85	84	86	91
$\Phi_{C\rightarrow O}$	0.41	0.2	0.12	

and frequency factor were obtained by Arrhenius treatment (Fig. 7).

The colouration/decolouration kinetics in a PVB film was considerably slower than in a PB72 film and the colourability was less pronounced (Fig. 8).

The quantum yield of the photocolouration reaction was determined by using the initial rate method which allowed the $\Phi_{C\rightarrow O} \times \varepsilon_O$ product to be determined. For the calculation of the quantum yield, the absorption coefficient of the coloured form was assumed to be the same as that determined in toluene (37600 dm^3 mol^{-1} cm^{-1}), where the absorption maximum of the coloured form (496 nm) is approximately at the same wavelength as in polymers. The reaction quantum yields obtained in both polymers along with the kinetic and thermodynamic parameters of the thermal bleaching, calculated by using the Eyring equation, are compared in Table 3 with those obtained in toluene.

4. Discussion

From the experiments described, it can be seen that the spectral features and photokinetic properties of Berry Red are very sensitive to the microenvironment. In solution, the dielectric and protic characteristics of the solvent, as well as its viscosity, are important factors in determining the chromatic and dynamic properties of the photochrome. In a polymer layer, local microviscosity and micropolarity can affect the dynamic behaviour by constraining the molecular movements and limiting free rotation, especially when the photoprocess is accompanied by significant structure and volume changes. Polarity and polarizability of the photochrome in the ground, as well as in the excited state, also have a role in determining the spectral patterns and dynamic behaviour.

In solution, the coloured form of Berry Red exhibits a notable positive solvatochromism (spectral red-shift with increasing the polarity of the solvent), which is due to increased polarity from the ground to the excited state. This behaviour, not frequently found for chromenes, has been previously reported for another structurally related compound [15] and indicates that the ground-state, weakly-polar, molecule should approach the configuration of the quinoid form. The positive solvatochromism is favoured by the electron-donating 4-methoxyphenyl groups [16].

Comparing the results in 3MP and toluene, the effect of the solvent on the photocolouration quantum yield is irrelevant, whereas the photobleaching yield is reduced by fifty times in 3MP ($\Phi_{\mathrm{O}\rightarrow\mathrm{C}} = 0.0006$ vs. 0.030 in toluene). This cannot be explained. The thermal bleaching rate constant in toluene is approximately reduced to a half of its value in 3MP. This enhances the colourability of Berry Red in toluene. As can be inferred from the data in Table 2, the slower bleaching rate in toluene is due to slightly higher activation energy in the temperature interval explored. The contrary would occur at low temperature where the entropy factor dominates.

The inclusion in polymer layers has the effect of lowering the energy barrier for the ring closure, especially in a PVB film where the barrier is reduced to a half of its value in a fluid organic solvent. Compared to solution, the lower energy barrier to closure, which was found in both films, appears as due to a catalytic effect induced by the polymer, which offers a lower energy path to the reaction. The pre-exponential factors are smaller in films than in solution and much more in PVB (Table 3). It is conceivable that a molecule with numerous flailing appendages, such as Berry Red, would have a long average time of approach to and crossing over the barrier. A cisoid intermediate in the closing process would lead to a more constrained structure and hence to a lower entropy in going from the reactant to the intermediate. This is reflected in the negative values of activation entropy in polymer films (Table 3) which can be related to the molecular rearrangement to the activated complex structure. This rearrangement in solid phase does not allow free intramolecular rotation, due to a restriction of freedom for the ring-closing reaction. Conversion of vibrational/rotational energy into heat can favour the crossing of the barrier. The T_g is considered an important parameter for the movement of the photochromic system in a polymer matrix. Here, the T_g is higher for the PVB film (∼60 °C) than for the PB72 film (∼40 °C), in agreement with the higher frequency factor determined in PB72. The latter film, which has a smaller elastic modulus, shows a higher reaction quantum yield that increases the photochromic performance. The complementary role of the energy and entropy factors results in the constancy of the activation free energy. The deviations from monoexponential bleaching kinetics, observed in PVB, are probably due to different closing rates of the coloured form in different local environments. A similar behaviour has been reported for some structurally related naphthopyrans [17] as well as for some spirooxazines [18] in sol–gel matrices and was attributed to different merocyanine conformations. This can also occur in the present case.

5. Summary and conclusions

It can be concluded that Berry Red is an easily colourable, thermally reversible, photochromic molecule whose coloured form shows a marked solvatochromic effect. Inclusion into polymeric matrices does not drastically alter its photochromic properties. In the present work an approach to a quantitative photokinetic study of a photochromic compound embedded in a polymer matrix is presented. The results obtained show that the photochemical and kinetic parameters change from those in solution and are different in the two polymers investigated, due to their different T_g and elastic modulus. The photocolouration quantum yield is appreciably reduced in polymeric films and the kinetic and thermodynamic parameters of the bleaching reaction are significantly altered. The matrix has the effect of lowering both the activation energy and the pre-exponential factor of thermal bleaching. These compensating effects make the bleaching rates in films close to those in solution. Both matrices have shown sufficient chain mobility and free volume to allow the change in molecular conformation occurring in the photochromic process.

Acknowledgements

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