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Effect of antenna porphyrins and phthalocyanines on the photochromism of benzospiropyrans in poly(methyl methacrylate) films

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Abstract

Photochromic materials have optical properties that change reversibly in response to irradiation. The benzospiropyran used in this work undergoes a transmission change of approximately 90% at 550 nm; however, a reasonable reaction rate for both the forward and reverse reaction is necessary for applications such as smart windows in buildings. The time constant for colorless spiropyrans to darken to the merocyanine form under ultraviolet radiation is of the order of 10 min, but the reverse reaction is very much slower. The objective of this work was to increase the reaction rate for the reverse bleaching reaction. This was achieved by modifying the benzospiropyran in a poly(methyl methacrylate) matrix by the addition of one of seven porphyrins or phthalocyanines. We report second-order rate constants obtained from the slope of the reciprocal of the maximum absorption amplitude vs. time. These constants characterize the initial reaction rate. Data taken with an FTIR spectrometer showed that every porphyrin increased the initial reaction rate, with phthalocyanine showing the fastest reversion rate, 21-fold that of the unmodified benzospiropyran. One vanadyl phthalocyanine showed an eight-fold increase. The effect on the visible reaction rate was determined using vanadyl phthalocyanines, and a particular vanadyl phthalocyanine increased the initial reaction rate by a factor of approximately three. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photochromism; Infrared spectra; Visible spectra; Transmission; Reaction rate; Kinetics; Benzospiropyran; Porphyrin; Phthalocyanine

1. Introduction

Organic photochromism is defined as the reversible color change of a molecule upon irradiation with UV or visible light [1]. The photoreaction between the species proceeds via electronically excited states and causes a change in molecular structure or conformation, thereby altering the absorption spectrum [2].

Many potential applications of photochromic dyes, either as passive or active devices, have been proposed. The former is related to the ability of the dye-containing materials to act as a transmission-controlling light valve, for example photochromic windows, eye-protecting glasses, privacy shields, optical switches [3,4] and pho-

tomasking or photoresisting components. The active devices are based on light-induced changes in the photochromic materials themselves, for example UV or visible dosimeters, rewritable near-field optical recording [5], reusable optical storage media [6], holographic optical storage [7,8], and self-developing photographic films.

Benzospiropyrans are interesting molecules showing photochromism. The structure of one particular member of this class is shown in Fig. 1. Photochromism in benzospiropyrans involves the reversible breaking of a C–O bond in the pyran ring to form a merocyanine structure. Mo et al. [9] reported on the photochromism of the spiropyrans dye 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro [2*H*-1-benzopyran-2,2'-(2*H*)-indole] (NSBP) in a poly(methyl methacrylate) (PMMA) and in a metal alkoxide matrix. The incorporation of the dye in matrices is important, since the mechanical properties and thermal

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Fig. 1. Photochromic transformation of NSBP.

^h The two last data points were dropped.

Table 2

Comparison of second-order visible results using a linear regression fit

Film	Rate constant ^a (min ⁻¹)	R^2	Initial amplitude
NSBP	0.00512	0.9997	2.514
VanN	0.0161	0.9992	1.327
VanP	0.01096	0.9995	1.886

^a These values were determined after one irradiation with 366-nm UV.

linear regression. The slopes of these graphs are the reaction rate constants. The data obtained from the plots are summarized in Table 1. The R^2 values can range from 0 to 1 and characterize the goodness of the least-squares fit. The data show that porphyrins and phthalocyanines affect the rate constant for NSBP. In every case, the porphyrin increases the rate of relaxation. The effect varies by a factor of 2–21, with phthalocyanine showing the fastest reversion rate. Vanadyl phthalocyanines show accelerations of six- to eight-fold. Simple porphyrins containing no metals are slower and molybdenyl porphyrins are approximately as slow as NSBP by itself. Fig. 2 shows a comparison with NSBP using the non-metal-containing dopants TPPH and TPPC. Fig. 3 shows the relatively fast vanadyl complexes, VanN and VanP. Fig. 4 shows the relatively slow molybdenyl complexes. In Figs. 2–4, significant deviations from linearity sometimes occur for times longer than those in the linear region. We will characterize these deviations by the term non-linear bleaching. Non-linear bleaching in the films examined in the infrared was associated with faster bleaching rates than those predicted from the second-order rate constants. Fig. 5 compares the very fast phthalocyanine to NSBP and a slow molybdenyl complex. Interestingly, films doped with molecules of comparable size, but different functionality, such as

Table 3

Comparison of second-order visible results of VanN repeat runs

	Rate constant (min ⁻¹)	R^2
Original	0.0161	0.9992
Repeat 1	0.0188	0.994 ^a
Repeat 2	0.0188	0.997 ^b
Repeat 3	0.0215	0.983 ^c

^a A plot of the data from this run as $1/A^{3/2}$ vs. time gave a linear correlation with $R^2=0.9998$.

^b A plot of the data from this run as $1/A^2$ vs. time gave a linear correlation with $R^2=0.9997$.

^c A plot of the data from this run as $1/A^2$ vs. time gave a linear correlation with $R^2=0.9998$.

anthracene, cholesterol or lactose, show curvature in these plots, as shown in Fig. 6. Attempts to find other linear relationships (time vs. $\log A_0/A$, $1/A^2$, $1/A^{1/2}$, and $1/A^{3/2}$) with these three materials were not successful. Furthermore, the reversion rate with these non-porphyrin, non-phthalocyanine-containing materials is much slower than the undoped NSBP film. In some cases, the film retains the purple color of the merocyanine form of NSBP for weeks.

In order to obtain good linear regressions, some data points were discarded, as indicated in the figures. For example, the last data point was omitted for the VanN fit and the last two data points were dropped for the VanP fit. The data points obtained near the end of the experiment have more inherent error than those at earlier times, particularly for the faster films.

The initial amplitude of the absorption is approximately consistent with the wt.% of the NSBP present in the film. Apparently, at this doping level, the porphyrins do not mask the spiropyran from the UV radiation to any significant degree. The exception was the phthalocyanine film, which showed an initial amplitude lower than expected.

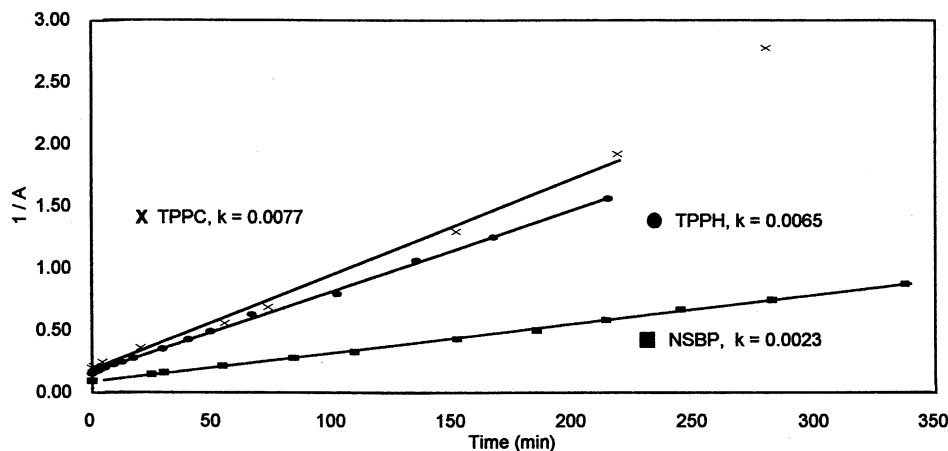


Fig. 2. Comparison of infrared second-order rate constants for NSBP, TPPH and TPPC.

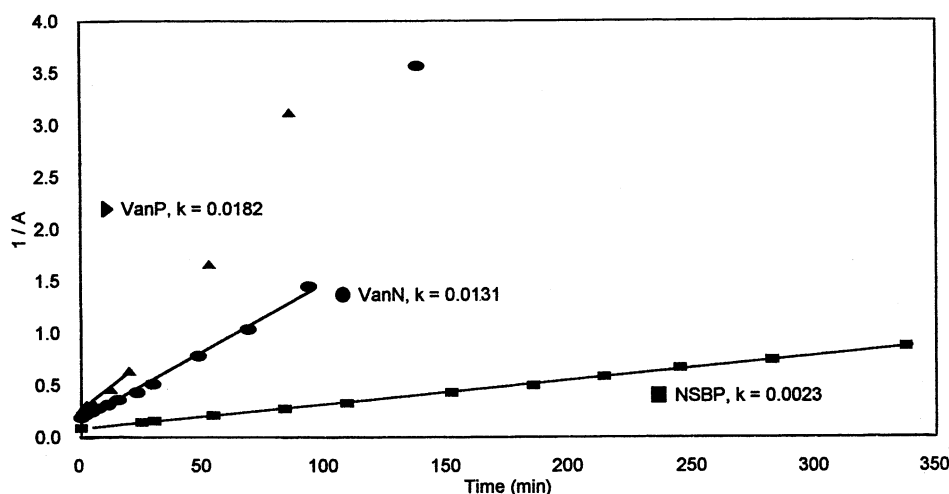


Fig. 3. Comparison of infrared second-order rate constants for NSBP, VanN and VanP.

NSBP, NSBP/VanN and NSBP/VanP were examined in the visible spectrum, as applications in this spectral range are the most promising. The values of λ_{\max} were 574.5 nm for NSBP, 574.5 nm for NSBP/VanN, and 578.3 nm for NSBP/VanP. Generally, these films show second-order behavior after initial irradiation with 366 nm UV, as shown in Table 2. Interestingly, the rate constant for the NSBP in the visible region is slightly more than two-fold greater than the corresponding rate constant given in Table 1 for the infrared. The VanP and VanN show the second-order rate constant increased by factors of approximately two and three, respectively. This means that the initial bleaching reaction occurs two- or three-fold faster with the phthalocyanines. Unlike the IR data, all the visible data are linear over the entire range. However, data in the visible range taken over a longer time may also show non-linear

bleaching. Thus, determination of the complete bleaching rate needed for applications in the visible region requires knowledge both of the linear information presented here and any non-linear bleaching that may occur at longer times. Interestingly, in the case of the VanN and VanP films, repeated irradiation shows approximately the same rate constant, although a small acceleration seems to be present after several irradiations, as shown in Table 3 for the NSBP/VanN films. Also, multiply irradiated films seem to show a better linear fit when plotted vs. $1/A^2$ or $1/A^{3/2}$ than vs. $1/A$.

We did not find it necessary to delete any data from the visible experiments to achieve linear fits. In contrast, the last few IR data points in a given run were frequently dropped to achieve a linear fit and characterize the initial reaction rate. If a given run in the visible region was not linear, as occurred upon multiple irradiation of

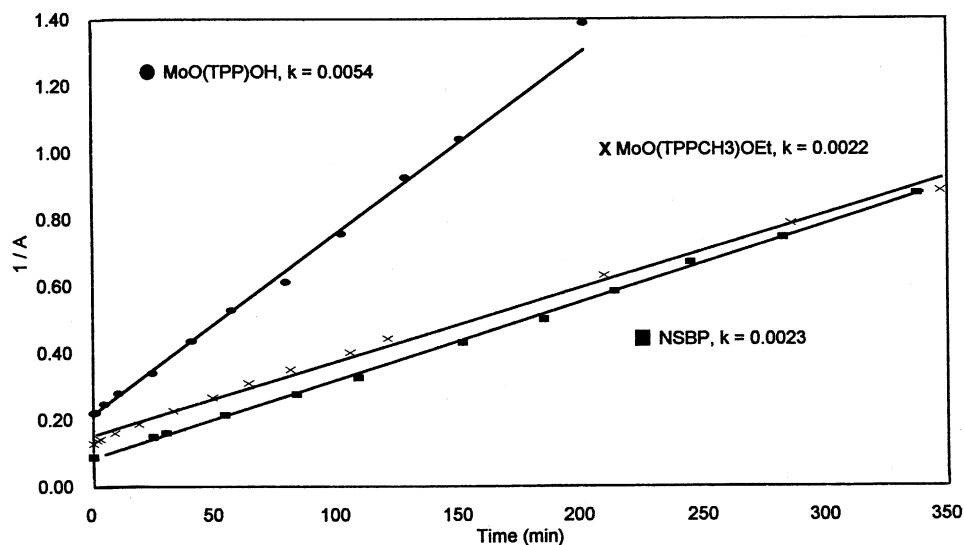


Fig. 4. Comparison of infrared second-order rate constants for NSBP, MoO(TPP)OH and MoO(TPPCH₃)OEt.

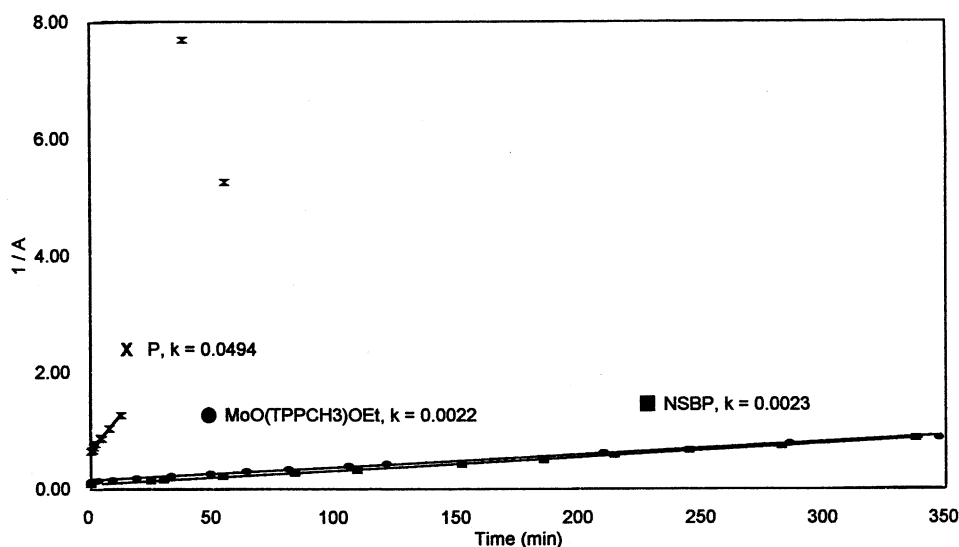


Fig. 5. Comparison of infrared second-order rate constants for NSBP, P, and MoO(TPPCH₃)OEt.

the VanN film, the deviation from linearity was obvious early in the data, whereas the deviation from linearity always occurred late in IR runs. Direct comparisons between the IR and visible data were not reliable for these reasons, particularly so in the VanP case, because the film reacted so quickly, and thus very few points were recorded in the IR region before non-linearity was obvious.

The rate enhancement observed for films doped with phthalocyanine is noteworthy and apparently unreported, but not, perhaps, unknown. A survey of the literature shows a number of recent patents, such as that by Perrott et al. [14], in which such combinations were used in films. However, to our knowledge, we are the first to

report quantitative rate constants in the infrared and visible regions. The ability of phthalocyanine and vanadyl phthalocyanines to form charge transfer complexes has been reported [15,16]. Phthalocyanine and porphyrins are also semiconductors. These properties might hint at the physico-chemical process that accelerates the photoreversion, and in particular explain why phthalocyanine and vanadyl phthalocyanines cause the greatest effect.

4. Conclusions

We have increased the initial reaction rate for the bleaching of a benzospiropyran film. This was achieved

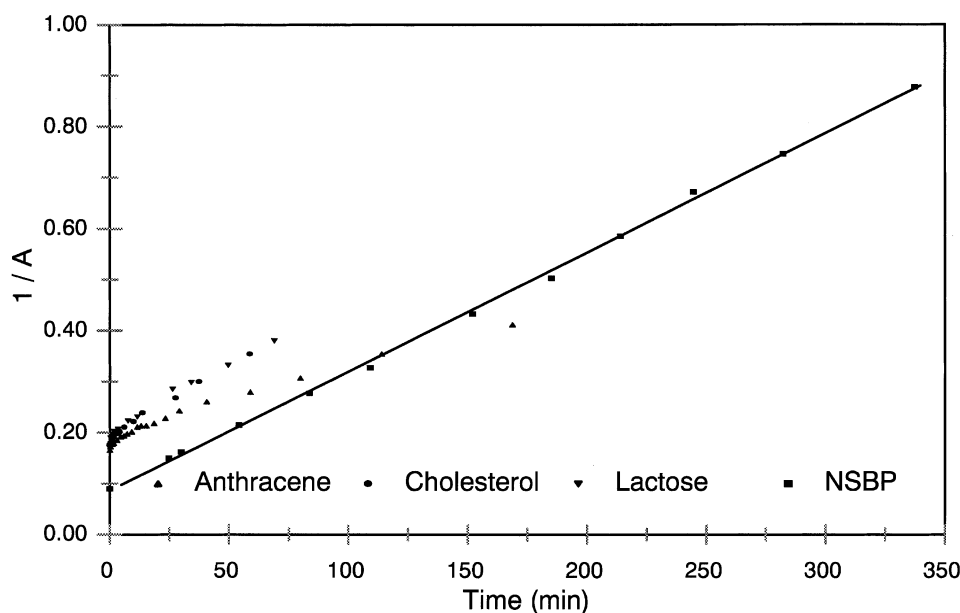


Fig. 6. Comparison of infrared second-order rate for anthracene, cholesterol and lactose, with NSBP.

by adding one of seven porphyrins or phthalocyanines to the benzospiropyran in a poly(methyl methacrylate) matrix. We have reported second-order rate constants obtained from the slope of the reciprocal of the maximum absorption amplitude vs. time. Data taken with an FTIR spectrometer showed that every porphyrin increased the initial reaction rate, with phthalocyanine showing the fastest reversion rate, 21-fold that of the unmodified benzospiropyran. Vanadyl phthalocyanines showed six- to eight-fold accelerations. We also detected non-linear bleaching that increased reaction rates in the infrared beyond the initial linear region. The effect on the visible reaction rate was determined using vanadyl phthalocyanines, and a particular vanadyl phthalocyanine increased the initial reaction rate by a factor of approximately three. Since data in the visible range taken over a longer time may also exhibit non-linear bleaching, complete characterization of the bleaching must then include the initial reaction rates reported here and any subsequent non-linear bleaching. The accelerations observed in the visible range in this preliminary work are not yet great enough for applications.

Acknowledgements

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