Formation of molecular H- and J-stacks by the spiropyran–merocyanine transformation in a polymer matrix

H. Eckhardt*, A. Bose and V. A. Krongauz†
Allied-Signal Inc., Corporate Technology, Morristown, NJ 07960, USA
(Received 11 December 1986; accepted 17 March 1987)

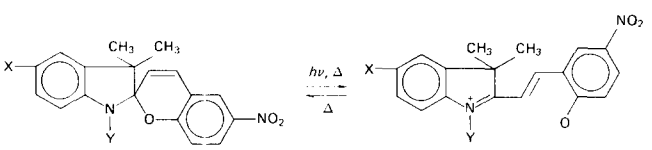
Kinetic and spectral properties of merocyanine dyes, formed on irradiation of spiropyran dissolved in a polymer matrix, depend on the spiropyran concentration. The observed properties are explained by a model in which the merocyanine molecules form molecular H-stacks. A method for formation of molecular J-stacks in the polymer matrix was also developed. Stabilization of the merocyanine dye in the J-stacks completely prevents the conversion back to spiropyran.

(Keywords: photochromics; thermochromics; spiropyran; H-stacks; J-stacks)

INTRODUCTION

Self-assembling of cyanine dyes into molecular aggregates has been the subject of great interest in the area of aggregate photoconductors[1,2]. This aggregation leads to the formation of ordered structures with very unusual physical properties. In many cases the molecular assemblies consist of stacks with deck-of-card type structures which dominate the electrical and optical properties of these aggregates. The absorption spectra of the stacks are usually red-shifted compared to isolated molecules, if the dipole–dipole interaction of molecules, forming the stacks, leads to a parallel orientation of dipoles (so-called J-stacks). In the case of antiparallel dipole interaction the spectra are shifted to the blue (H-stacks).

Recently the formation of molecular stacks and further aggregation were also observed by photo- and thermochromic transformation of spiropyrans into merocyanine dyes[3–5]:



Spiropyran Merocyanine

The stacking stabilizes the merocyanine form of the photochrome and gives rise to a variety of self-assembling materials. One aggregate, the so-called quasi-crystals, is formed on irradiation of spiropyran solutions in an electrostatic field followed by precipitation and consists of submicrometre-sized globules aligned in a 'string-of-beads' structure[6]. The globules are composed of highly dipolar cores (assemblies of J-stacks) covered by amorphous envelopes (H-stacks). The non-centrosymmetric structure of the cores results in optical nonlinearity of quasi-crystals with strong second-harmonic generation[7]. The relative content of J-stacks and H-stacks in the globules could be changed by variation of light intensity and temperature of the solution[8]. At very low temperatures (−100°C) the globules created on irradiation contained only H-stacks and could not be aligned in the string-of-beads structure in an electric field. They form only a colloidal solution.

Another example of assemblies is the H-stack formation of vinyl polymers with pendent spiropyran side groups in solution[9]. The absorption spectra of the photo-coloured solutions are shifted to the blue by 20 nm and the decolouration rates are retarded by more than an order of magnitude. The colour decay does not obey first-order kinetics and was described by a two-exponential function. Attempts to generate J-stacks only by this method failed.

There is no reason to believe that stack formation does not play an important role if the monomeric spiropyrans are dissolved in a solid matrix. Decolouration of merocyanines in polymers, for example, does not follow simple first-order kinetics and is accompanied by a hypsochromic shift of the absorption spectra (see ref. 10 and references therein). This has been attributed by some authors[11,12] to the existence of several merocyanine isomers with different fading rates. This assumption was criticized by Smets[10] who considered the complex kinetics to be a result of a non-homogeneous distribution of free volume in the polymer matrix. This explanation was also suggested earlier by other authors[13,14]. More recently Baessler and coworkers[15] have analysed the non-exponential time dependence of the merocyanine–spiropyran transformation in a copolymer in terms of a dispersive first-order chemical reaction. The last two models do not explain the spectral changes during the decolouration process, and neither of these models explains the retardation of the colour decay with reciprocal photochrome concentration[10].

In the present paper we report for the first time the formation of either J- or H- stacks of merocyanine on irradiation of spiropyran dissolved in polymer films.

* To whom correspondence should be addressed
† On sabbatical leave from the Weizmann Institute of Sciences, Department of Structural Chemistry, Rehovot, 76100, Israel

0032-3861/87/111959-06$03.00

Spectral properties, kinetic parameters and the structure of these stacks were studied. Our results make it clear that aggregation plays an important role in these systems and has to be considered along with the free-volume effect in the study of photochromic phenomena of spiropyrans in the solid phase.

EXPERIMENTAL

A 1:1 copolymer of isobutylmethacrylate and n-butylmethacrylate (Elvacite 2046), polystyrene (Aldrich), polymethylmethacrylate (PMMA) (Aldrich) and a spiropyran with X = Cl and Y = CH_3 (Chromadye 5 from Chroma Chemicals) were used without further purification. Thin films for spectroscopic and kinetic measurements were prepared by casting on a glass slide from a viscous xylene solution containing 30% of polymer and 1.5, 5 and 15% spiropyran relative to the weight of polymer. Uniform film thicknesses of 1–4 μm were achieved through the use of a wound stainless-steel rod ('Laneta Wire Caters' from Pacific Scientific). Two different methods of film preparation were applied to produce photochromes with different optical and kinetic properties:

(A) A film was cast and dried carefully and then irradiated to produce the merocyanine form.

(B) Irradiation with 366 nm u.v. light (Mineral lamp UVGL-25) started immediately after casting the film and continued for several minutes until the films were dry.

The films prepared by method B turned deep blue immediately and did not appear to fade for many days at room temperature in the solid phase. Films of type A were colourless. All films were dried further in vacuum for several hours to remove traces of solvent. Films for transmission electron microscopy (TEM) were cast on carbon-coated mica. The polymer concentration used for these films was lower to obtain thinner films for TEM ($\sim$0.5 μm). They were transferred to a grid on a water surface.

Spectral and kinetic data were obtained with a Perkin–Elmer 330 u.v.-visible spectrophotometer controlled by a PE 3600 data station. The data were transferred to a VAX 785 for nonlinear regression analysis using the SAS statistical package.

A Leitz Orthoplan polarizing microscope and a Hitachi H800 electron microscope were used for optical and electron microscopy.

RESULTS

Spectra and kinetic measurements

The polymer films prepared by method A (called A-films here) were colourless, but turned deep blue under 366 nm irradiation, which changed to violet upon fading. The films prepared by method B developed a deep blue colour under irradiation during solvent evaporation. The colour did not fade with time and was stable up to about 70°C. At temperatures around 100°C the colour disappeared slowly, possibly due to irreversible decomposition of the dye as indicated by a slight brown colour. The bleached films could not be converted into the coloured form again.

Spectra of the coloured films are shown in *Figure 1* together with a solution spectrum. A-film spectra are shifted to the blue compared to the spectrum of spiropyran in tetrahydrofuran (THF). The opposite is true for B-films which were irradiated during solvent evaporation. They exhibit a profound bathochromic shift. The hypsochromic shift of the spectra of photo-coloured A-films is more pronounced at higher spiropyran concentration. The absorption maxima shift further to the blue during colour fading (*Figure 2*), indicating that the longer-living species absorb at shorter wavelengths. The rate of colour decay depends on the spiropyran concentration in the films and does not obey first-order kinetics. This is demonstrated in *Figure 3* where the normalized optical density at constant wavelength is plotted *versus* time. The full curves represent two-exponential fits to the data points. The rate constants deduced from equation (3)—see later—show that the lifetime of the transient merocyanine species increases with increasing spiropyran concentration (see *Table 1*).

Optical and electron microscopy

Viewed under the optical microscope the A-films look homogeneous and there appears to be no morphological difference from the polymer films without spiropyran. In

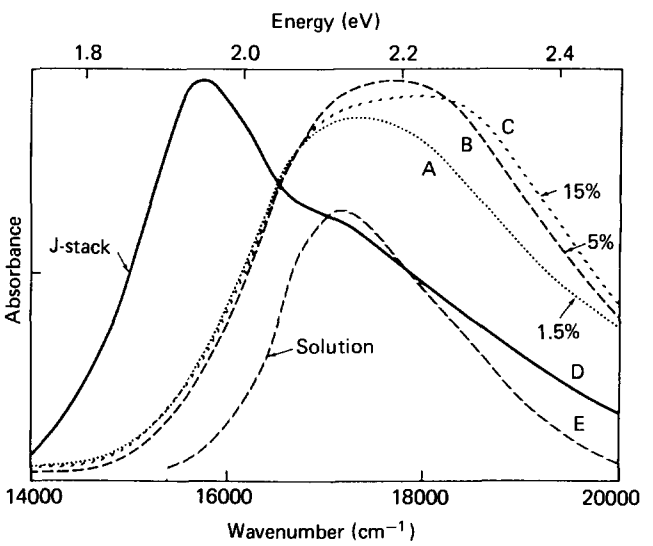


Figure 1 Spectra of spiropyran in films (25°C) and solution (4°C) taken 1 min after irradiation: A, 1.5% spropyran in polymer film; B, 5% spiropyran; C, 15% spiropyran; D, spectrum of 5% spiropyran film irradiated immediately after casting, during solvent evaporation; E, 1% solution in THF

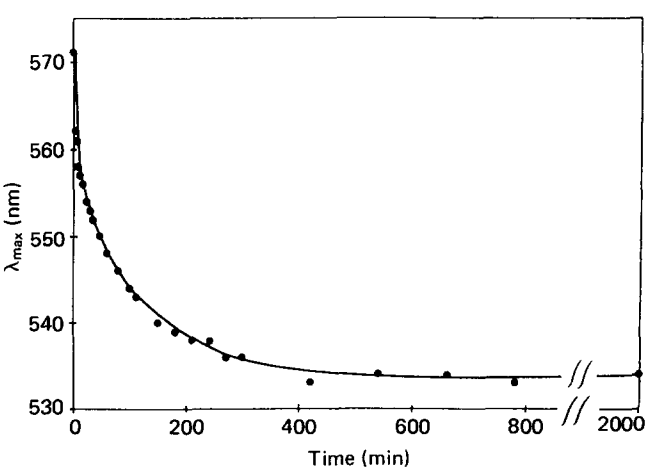


Figure 2 Spectral shift of 5% A-film during colour decay

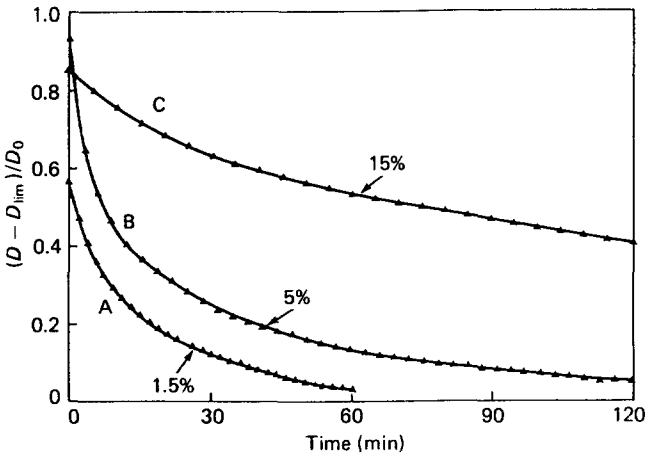


Figure 3 Kinetics of colour decay: A, film with 1.5% spiropyran; B, 5% spiropyran; C, 15% spiropyran. Absorbance measured at 555 nm. Full curves represent fits of data points using equation (3)

Table 1 Calculated decay parameters for films with different spiropyran concentrations in the copolymer using equation (3). The absorbance was recorded at 555 nm

Concentration of spiropyran (%)	α_1	α_2	k_1 (s^{-1})	k_2 (s^{-1})
1.5	0.038	0.115	0.0045	0.0007
5	0.051	0.117	0.0022	0.0002
15	0.177	0.652	0.0008	0.00007

contrast, the B-films are heterogeneous and contain blue aggregates up to 5 μm in diameter (*Figure 4*). These aggregates exhibit birefringence under crossed polars.

The fine structure of the aggregates is clearly visible under the transmission electron microscope. They are composed of thin fibres (see *Figure 5*) of $\approx$200 Å diameter. We could not observe any distinct electron diffraction from these aggregates or from the A-films.

Low-angle X-ray diffraction from the B-films gives the same diffuse scattering as the polymer matrix. There is no indication of crystalline order in the aggregates.

Temperature dependence

The temperature dependence of both rate constants is of the Arrhenius type over the range 5 to 25°C. An activation energy of 18.5 kcal mol^{-1} for k_2 and 17.5 kcal mol^{-1} for k_1 is deduced from *Figure 6*. Similar results were reported by Smets[10].

Influence of polymer matrix and composition of spiropyran

The kinetic constants in *Table 2* give some indication of the effect of various polymer matrices on the kinetic properties.

DISCUSSION

The ability of merocyanine dyes to aggregate into large molecular stacks is well documented[1]. Previously we have shown that the observed hypsochromic shift of absorption spectra of merocyanines in solution formed in the photochromic reaction and the retardation of the thermal merocyanine–spiropyran conversion can be attributed to H-stack formation of merocyanine molecules[9]. Similar blue shifts and retardation of colour fading are observed for our irradiated A-films (see *Figures 1, 2* and *3*) with higher spiropyran concentration. This is a clear indication that H-stack formation occurs in our polymer films. The absorption spectrum of the low-concentration (1.5%) film has a maximum close to the maximum of the solution spectrum. For higher concentration the maxima are shifted to the blue by 20 to 30 nm. The magnitude and the direction of these shifts is typical for H-stack formation. Since merocyanine molecules do not associate in THF[9] and the absorption maximum of the 1.5% film is close to the maximum of the solution spectrum, one can conclude that aggregation of merocyanines is less significant at lower concentration. This is consistent with the higher fading rate of the 1.5% film.

Earlier, Verborgt and Smets[16] observed a less pronounced retardation of merocyanine–spiropyran conversion in PMMA films, but did not discuss the mechanism of the effect.

To explain the retardation of colour decay and blue shift of absorption spectra in solutions of merocyanine H-stacks, a model was proposed in which the edge merocyanine molecules in a stack of length n are converted to spiropyran first, i.e. the conversion occurs step-by-step from the ends of the stack[17]. Since the decolouration rates for shorter stacks are larger, the shorter stacks disappear first. This mechanism leads to an increase of concentration of longer stacks in the system and shifts the average stack length to longer stacks with time. The observed shifts in absorption maxima (*Figure 2*) are consistent with this mechanism. For the A-film with 5% spiropyran, for example, the absorption maximum of the first spectrum ($t = 0$) is shifted by 20–25 nm to the blue compared to the solution case. As the H-stacks decay the maxima shift further to the blue by 20–25 nm.

The large spectral shifts in dye aggregates are usually explained by the semiquantitative molecular exciton model. This dipole theory predicts a red shift relative to the monomer for J-stacks and a blue shift for H-stacks[18]. In the framework of this theory the hypsochromic shift of

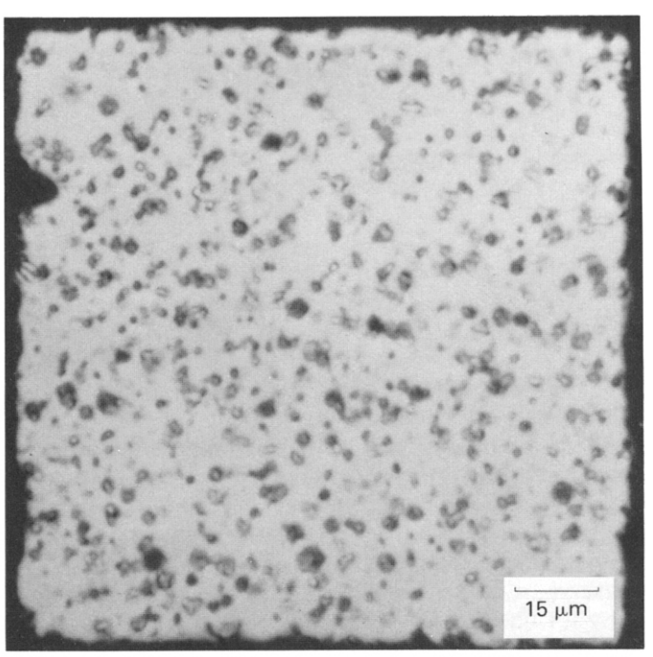


Figure 4 Optical micrograph of a B-film

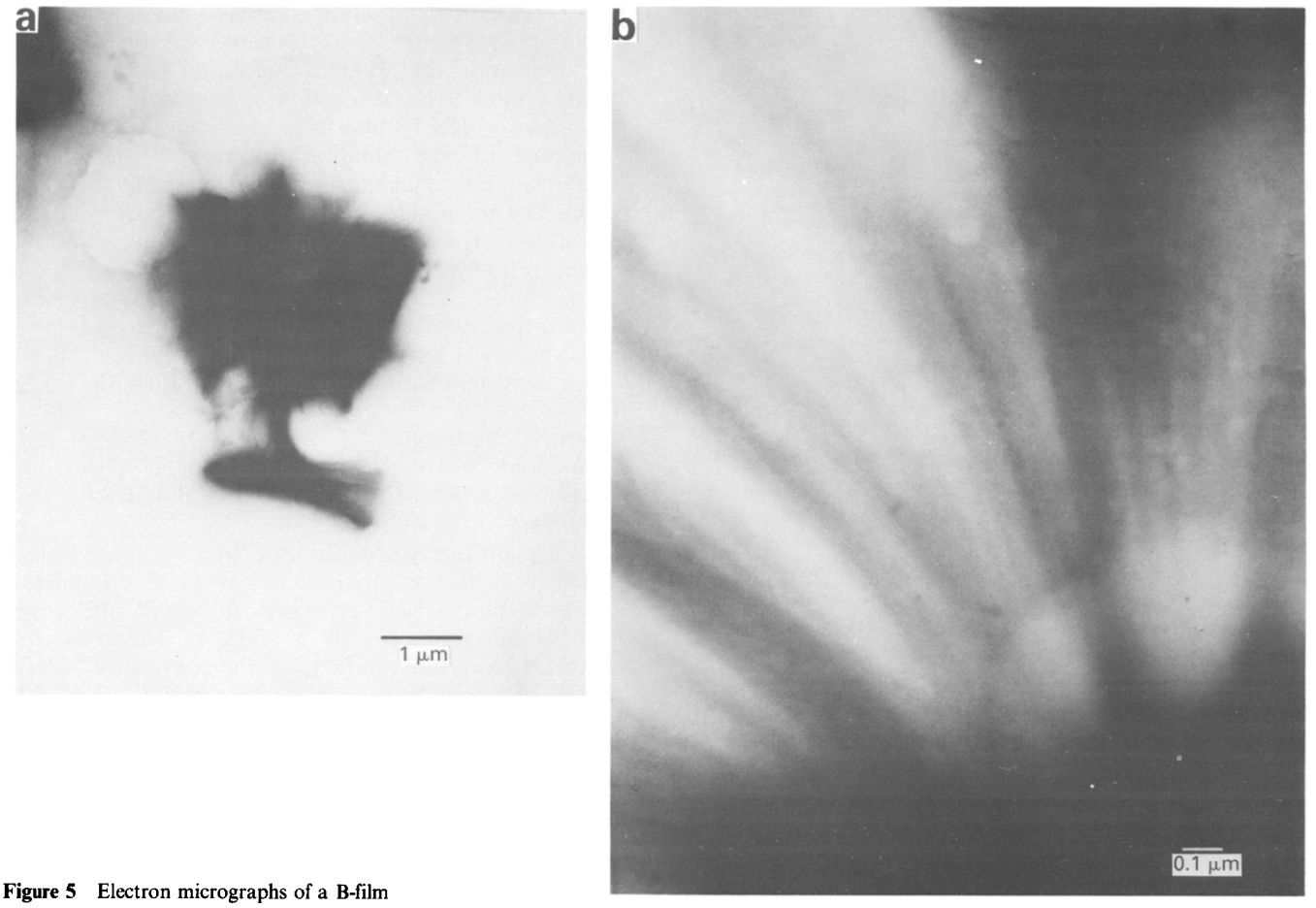


Figure 5 Electron micrographs of a B-film

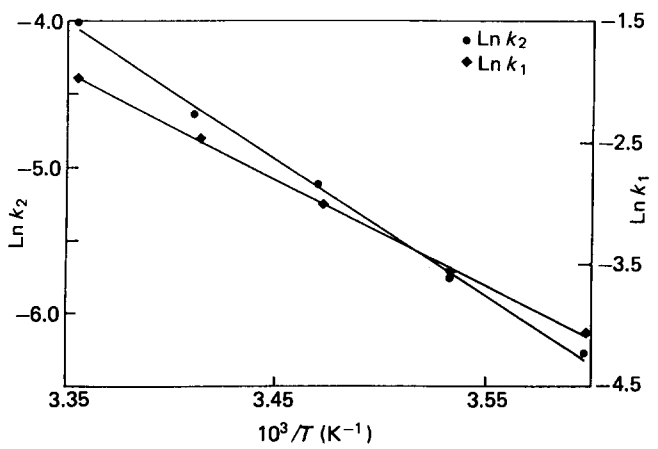


Figure 6 Temperature dependence of rate constants

H-stacks is given by

$$\Delta\nu_{(n\text{-monomer})}=\frac{2(n-1)\langle m^2\rangle}{hnr^2}(1-3\cos^2\alpha) \qquad (1)$$

where $\Delta\nu$ is the spectral shift from the monomer absorption, h is Planck's constant, $\langle m^2\rangle$ is the transition dipole moment of the monomer, r the separation of molecular centres, α the tilt angle between the line of centres and long molecular axes, and n is the degree of aggregation. As can be seen from (1) the monomer-to-dimer spectral shift should account for half of the observed shift for $n\rightarrow\infty$ assuming that other parameters are not changing with n. For $n\geq 5$ the dependence of absorption maxima on n can practically be neglected. In our case the spectrum of the non-associated merocyanine molecules in THF had a λ_{max} of 585 nm, while the absorption of the largest stacks, which dominate the spectrum after long times, peaks at $\lambda_{max}=535$ nm ($\Delta\lambda=50$ nm) (*Figure 2*).

We conclude therefore that the starting spectra of films with 5 and 15% spiropyran concentration ($\lambda_{max}=560$ nm and $\Delta\lambda=25$ nm with respect to solution maxima) have a significant contribution of dimer absorption. The distribution of stack lengths in the film leads to an overlap of spectra of stacks with different n and to a broadening of the entire absorption spectrum. This makes it very difficult to deduce the contribution of a particular stack to the absorption or the concentration of a particular stack n in the film. Apparently, monomer absorption contributes mostly to the absorption spectrum of the 1.5% film ($\lambda_{max}=580$ nm, $\Delta\lambda=5$ nm).

If we assume that the fading process is a result of consecutive transformation of longer stacks into shorter ones and, in a final step, into spiropyran, we can describe the optical density D at wavelength λ as the following function of time:

$$D/D_0=\alpha_1 e^{-k_1 t}+\alpha_2 e^{-k_2 t}+\ldots+\alpha_n e^{-k_n t} \qquad (2)$$

Here $k_1, k_2, \ldots, k_n$ are the decay rate constants of stacks with $n=1, 2, \ldots, n$, and $\alpha_1, \alpha_2, \ldots, \alpha_n$ are the contributions of these stacks to the absorption at wavelength λ (α is a function of λ). D_0 is the absorption at $t=0$. Since $k_1>k_2\ldots>k_n$ we can, in a first approximation, describe the initial kinetics (first 2–3 h) by a two-exponential function with only two terms making a major contribution to the absorption change and by a

constant D_{lim} which takes contributions from stacks with higher n into account:

$$(D-D_{lim})/D_0=\alpha_1 e^{-k_1 t}+\alpha_2 e^{-k_2 t} \quad (3)$$

Here α_1 and α_2 are the fractions of merocyanine moieties which decay with rate constants k_1 and k_2 respectively. The two-exponential approximation gives good agreement with the experimental results (see *Figure 3*) and allows us to estimate roughly the kinetic parameters of the films.

The retardation of the colour decay with increasing stack length is illustrated in *Table 1*. Assuming that the stack size is proportional to the spiropyran concentration and that only the end merocyanine molecules in a stack are converted into spiropyran, one can expect the decay rate to depend inversely on the spiropyran concentration[17]. This is indeed observed (*Figure 7*) for all rate constants except k_1 for the lowest concentration which is the case of non-associated merocyanines. As expected for the free molecule the decay rate constant becomes independent of concentration.

Our experimental results do not allow us to resolve the kinetic characteristics of merocyanine H-stacks with different length n because of the strong overlap of the absorption bands. Nevertheless, comparing the spectral and kinetic data it is possible to conclude that the non-associated merocyanine molecules dominate the decolouration process and the spectra of films with a 1.5% spiropyran at the beginning of the colour decay, while the dimers dominate after 10–15 min. The contribution of dimers in 5% films is substantial at the very beginning and trimers become important after about 30 min (*Figures 2* and *3*). It should be emphasized again that after 2–3 h the decay of tetramers or even pentamers may be important, but the contribution of these moieties to the total absorption is significant only for the higher concentrations of spiropyran (15%) and is described by D_{lim} in our analysis.

From *Table 2* a slight dependence of k_1 on the polymer matrix can be seen. Assuming that the polarity of the matrix increases in the order polystyrene < copolymer < PMMA one can conclude that decay of monomeric merocyanine molecules, characterized by k_1, is slower in more polar matrices in agreement with results reported earlier[9]. Decay of dimers (k_2) does not show an explicit trend.

Even though the association of the merocyanine molecules in H-stacks is apparently small it is not clear yet

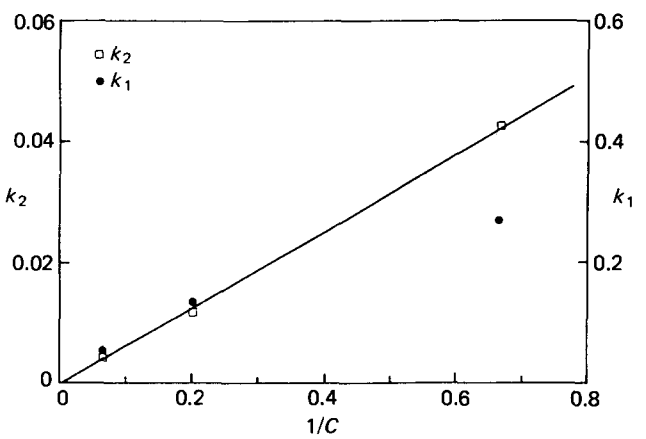


Figure 7 Dependence of rate constants on spiropyran concentration (rate constants in min^{-1})

Table 2 Comparison of kinetic parameters for colour fading of 5-chloro-6-nitro-BIPS[a] in different polymer matrices at room temperature (two-exponential fit). The concentration is 5%

Polymer	k_1 (s^{-1})	k_2 (s^{-1})
Copolymer	0.00223	0.0002
Polystyrene	0.00542	0.00055
PMMA	0.00165	0.00045

[a] BIPS = 1',3',3'-trimethylspiro-[^{2}H-1-benzopyran-2,2'-indoline]

how this association occurs in the rigid polymer matrix. One assumption is that the close spacing of merocyanine molecules necessary for stack formation is provided by possible aggregation of spiropyran molecules during solvent evaporation after casting of the films from the polymer solution. However, the u.v. spectra of non-irradiated A-films did not show any significant difference from spectra of spiropyran in xylene. Clearly, more work is needed to address this question.

Spectral and microscopic investigations of the B-films reveal a quite different picture. Irradiation of the wet films leads to aggregation of the merocyanine dye into gigantic J-stacks which are phase-separated in the polymer matrix. The aggregates do not give discrete electron and X-ray diffraction indicating the absence of a long-range crystalline order. However the distinct birefringence confirms a certain regularity in their structure. Usually, J-stacks in solution have a red-shifted absorption spectrum with a narrow bandwidth. The same is observed for our J-stacks in a polymer matrix. The narrower bandwidth indicates that the J-stacks are much longer than the H-stacks and the distribution of stack lengths is narrower. The pictures obtained by optical and electron microscopy are similar to pictures seen for other cyanine dyes aggregated in solution[19] and a thiapyrylium dye in a polymer matrix[2]. The question why the higher degree of aggregation, leading most likely to the phase separation, results in J-stacks rather than H-stacks remains still open.

CONCLUSIONS

We have shown that the spectral and kinetic properties of photochromic spiropyrans in a polymer matrix depend on molecular association of the merocyanine dye. The type and degree of association can be controlled by changing the conditions for film preparation. At low degree of association the merocyanine molecules are organized in a rather loose H-stack structure which allows thermal conversion back to the spiropyrans. Retardation of this back-reaction as well as the hypsochromic shift depend on the degree of association.

The J-stack formation leads to a high degree of merocyanine association, a bathochromic spectral shift and phase separation of the J-stacks embedded in the polymer matrix. Stabilization of the merocyanine form in J-stacks is so strong that the dye appears to be indefinitely stable and cannot be converted to spiropyrans without degradation. This stabilization is connected to the strong interactions between merocyanine molecules in J-stacks and the regular structure of J-aggregates.

The observed aggregation phenomena are not limited to the particular spiropyran and polymer matrix used in our study. The tendency of merocyanine molecules to form stacks is so strong, at least at higher concentrations, that one would expect aggregation to be a dominant

factor in all photochromic phenomena involving spiropyrans in the solid phase.

ACKNOWLEDGEMENTS

We thank V. Kramer for taking the electron micrographs and S. Murthy for help with X-ray diffraction.

REFERENCES

1 Sturmer, D. M. and Heseltine, D. W. in 'The Theory of the Photographic Process', (Ed. H. Jammes), Macmillan, New York, 1977, Ch. 7 and 8
2 Perlstein, J. H. in 'Electrical Properties of Polymers', (Ed. D. A. Seymor), Academic Press, 1982, Ch. 2
3 Krongauz, V. A. *Israel J. Chem.* 1979, **18**, 304
4 Krongauz, V. A. and Goldburt, E. S. *Macromolecules* 1981, **14**, 1382
5 Cabrera, I., Shvartsman, F., Weinberg, O. and Krongauz, V. A. *Science* 1984, **226**, 341
6 Krongauz, V. A., Fishman, S. N. and Goldburt, E. S. *J. Phys. Chem.* 1978, **82**, 2469
7 Meredith, G. R., Williams, D. J., Fishman, S. N., Goldburt, E. S. and Krongauz, V. A. *J. Phys. Chem.* 1983, **87**, 1697
8 Parshutkin, A. A. and Krongauz, V. A. *Mol. Photochem.* 1974, **6**, 437
9 Goldburt, E. S., Shvartsman, F. P., Fishman, S. P. and Krongauz, V. A. *Macromolecules* 1984, **17**, 1225; Goldburt, E. S., Shvartsman, F. P. and Krongauz, V. A. *Macromolecules* 1984, **17**, 1876
10 Smets, G. *Adv. Polym. Sci.* 1983, **50**, 17
11 Heiligman-Rim, R., Hirshberg, Y. and Fischer, E. *J. Phys. Chem.* 1962, **66**, 2465; 2470
12 Arnaud, J., Wippler, C. and Beaure D'Augeres, F. *J. Chim. Phys.* 1967, **64**, 1165
13 Kryszewski, M. and Nadolski, B. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 345
14 Eisenbach, C. D. *Polym. Bull. (Berlin)* 1980, **2**, 169; *Ber. Bunsenges. Phys. Chem.* 1980, **84**, 680
15 Richert, R. and Baessler, H. *Chem. Phys. Lett.* 1985, **116**, 302
16 Verborgt, J. and Smets, G. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 2511
17 Goldburt, E. S. and Krongauz, V. A. *Macromolecules* 1986, **19**, 246
18 McRae, E. D. and Kasha, M. 'Physical Processes in Radiation Biology', Academic Press, New York, 1964, pp. 23–42
19 Emerson, E. S., Conlin, M. A., Rosenoff, A. E., Norland, K. S., Rodriguez, H., Chin, D. and Bird, G. R. *J. Phys. Chem.* 1967, **71**, 239