LASER PHOTOLYSIS STUDIES OF THE LIGHT-INDUCED FORMATION OF SPIROPYRAN–MEROCYANINE COMPLEXES IN SOLUTION
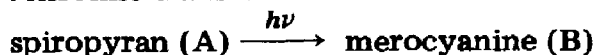
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Summary

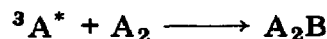The kinetics of formation of the complexes AB and A_2B during the photochromic transformation

$$\text{spiropyran (A)} \xrightarrow{h\nu} \text{merocyanine (B)}$$

in solution was studied by the laser flash photolysis technique. It is concluded that the complexes are formed in the reactions

$$A_2 \xrightarrow{h\nu} AB$$

and

$$^3A^* + A_2 \longrightarrow A_2B$$
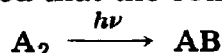
thus implying the presence of dimers A_2 in solution. The effect of the kinetics of these reactions on the composition of globules of quasi-crystalline dispersions is discussed.

1. Introduction

In earlier studies it has been shown [1 - 6] that colloidal dispersions are formed during the photochemical transformation of photochromic spiropyrans dissolved in aliphatic hydrocarbons (see Fig. 1). The dispersions con-
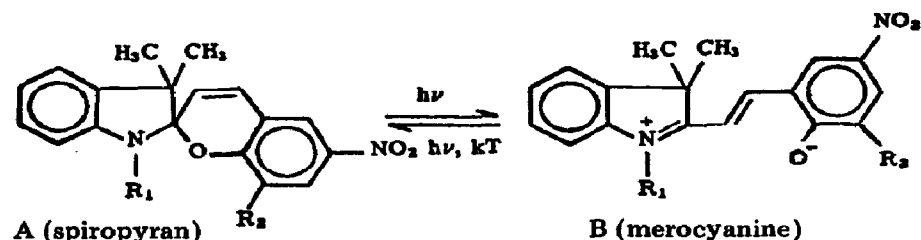

Fig. 1. The photochemical transformation of photochromic spiropyrans.

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sist of spherical particles (globules) approximately 0.1 - 0.4 μm in diameter. The globules in turn consist of crystalline nuclei covered by amorphous envelopes. The nuclei, which are composed of microcrystals, reveal optical and electrical anisotropy; they have permanent dipole moments greater than 10^4 debye. This causes remarkable properties of the dispersions. The globules form string-of-beads structures in a constant external electric field. Macroscopically these strings look like coloured threads aligned along the electric lines of force. The threads exhibit linear optical dichroism due to orientation of the crystalline nuclei along the field. Some features of the globules and threads are inherent in crystals and some are typical of liquids. The threads have been termed quasi-crystals.

The absorption spectra of the nuclei are shifted by about 100 nm compared with those of the amorphous envelopes [2, 3]. This has been ascribed to the difference in chemical composition of amorphous and crystalline material. On irradiation with very intense light, or at temperatures lower than 180 K, the dispersions formed are composed only of amorphous material which has been shown to consist of A and B in the stoichiometric ratio 1:1. It has been demonstrated [2] that molecules A and B combine in solution to form complexes AB prior to the formation of the dispersion.

The crystalline nuclei have been shown to contain A and B in the ratio of approximately 2.5:1, apparently due to the formation of the complexes A_2B or A_3B. The method of estimation of the ratio A:B has not allowed us to distinguish between the forms A_2B and A_3B and, therefore, the formula A_nB (with n = 2 - 3) has been used.

The following scheme for globule formation has been suggested to explain the experimental data. The merocyanine molecules B produced during irradiation of spiropyran in solutions of aliphatic hydrocarbons combine with the spiropyran molecules A to form dimers AB. The latter can then react with other molecules of A, resulting in the highly polar complexes A_nB. This reaction demands an activation energy and, hence, is retarded when the temperature is decreased. The dimers AB can also combine with each other to give an amorphous material. This process competes with A_nB formation and is favoured by high light intensity and low temperatures.

Once the polar complexes A_nB are formed, they can also aggregate to give dipolar molecular stacks similar to the J or Scheibe stacks inherent in many cyanine dyes. The stacks in turn form three-dimensional highly dipolar microcrystals. Coating of these microcrystals by the non-polar amorphous material creates a colloidal dispersion of globules in non-polar solvents.

All stages of globule growth have been followed directly in the electron microscope, *i.e.* the formation of microcrystals from molecular stacks, their consolidation into globular nuclei and their coating by amorphous material. However, we have not been able to observe directly the processes preceding the separation of the new phase, in particular the formation of the complexes AB and A_nB, and therefore the proposed scheme of AB and A_nB formation has been considered only as a working hypothesis.

This work is devoted to the direct investigation of these primary chemical processes by use of the laser flash photolysis technique.

A conventional flash photolysis investigation of the primary processes in the phototransformation of spiropyrans in aliphatic hydrocarbon solutions has been carried out by Bercovici *et al.* [7]. These authors have found that colouration of aerated solutions is instantaneous, *i.e.* no intermediate with a lifetime beyond the duration of the flash ($20 \, \mu s$) could be detected. In evacuated solutions a fraction of the colour is also formed within the duration of the flash but an additional colouration in the region 500 - 600 nm appears after the flash during about 20 - 30 μs. The peak at 430 nm formed during the flash decays at the same rate. A third fraction of the colour is formed within several milliseconds. The form of the spectral band in the region 500 - 630 nm is changed during the increase of the absorption after the flash, indicating that the spectrum is a superposition of at least two entities which are treated as different stereoisomers of the merocyanine form B. The transient with $\lambda_{max} = 430$ nm is quenched by oxygen and is considered to be a triplet state of the spiropyran molecule which is responsible for the formation of a part of the Bs in the following sequence:

$$^1A^* \to {}^3A^* \to B_1 \to B_2 \ldots$$
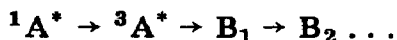
A transient which absorbs at about 430 - 450 nm, which is quenched by oxygen and with a lifetime of about 5×10^{-4} s has also been observed in toluene by Mosse and Metras [8]. These authors have also concluded that this is a triplet state of A which converts into B.

Now we know that the colour in the aliphatic hydrocarbons is caused by the complexes AB and $A_n B$ which form the colloidal dispersion even at spiropyran concentrations below 10^{-4} M. Presumably the triplet molecules A convert eventually to one or both of these complexes.

2. Experimental

6-Nitro-1',3',3'-trimethylspiro([2*H*-1]-benzo-pyran-2,2'-indoline) [9] (Nitro-BIPS) was prepared by Mr. M. Kaganovich and purified by recrystallization. Spectrograde solvents were used without further purification. Low concentrations of Nitro-BIPS (1.3×10^{-4} - 7×10^{-6} M) were used both to avoid separation of the colloidal phase and to obtain uniform absorption of the laser light ($\lambda = 347.1$ nm).

The micellar solutions of Nitro-BIPS were prepared by mixing a 1.3×10^{-5} M stock solution in isopentane with aqueous solutions of surfactants (10^{-2} M CTAB or 2% Triton). The resulting solution was bubbled with nitrogen for 2 h to remove the isopentane. The irradiations were carried out in a nitrogen atmosphere.

The ruby laser flash photolysis system has been described elsewhere [10]. The wavelength used was 347.1 nm and the pulse duration was about 25 ns. The light intensity of the laser pulse was varied by placing BG23 Schott filters in the beam.

3. Results

At each wavelength in the range 450 - 680 nm the absorption was measured as a function of time after the laser flash (halfwidth about 25 ns). Four representative oscillograms are shown in Fig. 2. The initial fast rise in
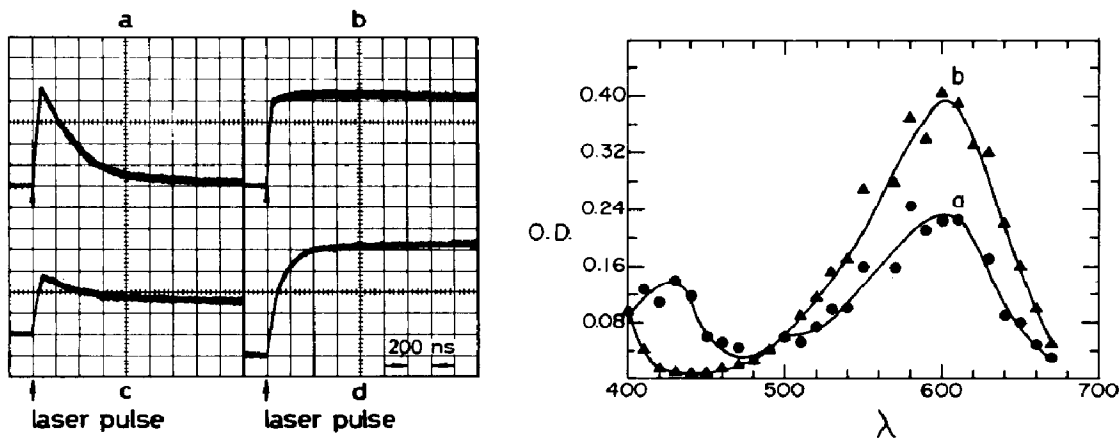

Fig. 2. Oscillograms obtained at various wavelengths: (a) 430 nm; (b) 500 nm; (c) 460 nm; (d) 600 nm. The concentration of Nitro-BIPS in methylcyclohexane was 1.3 × 10⁻⁴ M.

Fig. 3. Absorption spectra observed after the laser flash, obtained from oscillograms similar to those in Fig. 2: curve a, complete spectrum approximately 60 ns after the start of the flash; curve b, the spectrum after 2 μs ("long-lived products").

curves a, b and c, *i.e.* for wavelengths below 520 nm, corresponds to the duration of the laser flash, so that the absorption at time (for example) 50 - 70 ns is caused by a species formed within the duration of the flash. The curves between 600 and 680 nm are similar to that given in Fig. 2(d). At wavelengths in the range 520 - 580 nm a superposition is observed of a very fast initial rise, as in curve b of Fig. 2, and a further slow rise to a quasi-stable absorption (actually having a half-life of about 1 s). The results can be interpreted as follows. The observations in the range 450 - 480 nm indicate that a transient "X" is formed "instantaneously" and decays by a first order reaction with $k = (6 \pm 1) \times 10^6$ s⁻¹ (Fig. 2(a)).The observations at wavelengths above 460 nm show another transient "Y", which is also formed instantaneously but which is practically stable on the time scale used (Fig. 2(b)). Curve a in Fig. 3, based on absorbance values 60 ns after starting the laser pulse, gives an indication of the absorption curve of the "X" and "Y" transients. The transient "Y" is, however, overlapping strongly with transient "Z" in the range of about 520 - 580 nm. Transient "Z" is formed at a rate similar to that of the decay of "X" (Fig. 2(d)), indicating a reaction X → Z. It absorbs in the range 520 - 680 nm and is also practically stable on the time scale used. Curve b in Fig. 3, taken about 1 μs after the flash, represents a superposition of the absorption spectra of "Y" and "Z" in the final propor-tion between the two, whilst in curve a the contribution of species "Z" is

smaller. Obviously it is difficult to estimate the absorbance of each of the three species X, Y and Z in the spectral ranges where their spectra overlap strongly.

Spectrum b (Fig. 3) is similar to the spectra of colloidal dispersions of quasi-crystalline globules and threads [3]. It has been shown that the band at 600 nm can be attributed to the polar complexes A_nB which form crystalline nuclei, whilst the band with a maximum near 500 nm is caused by dimers AB in the amorphous envelopes. We can therefore assume that, of the two long-lived species formed by the laser pulse, "Y" is AB and "Z" is A_nB.

Relative optical densities of all three species (430, 500 and 600 nm) as a function of the laser pulse intensity are shown in Fig. 4. Apart from the
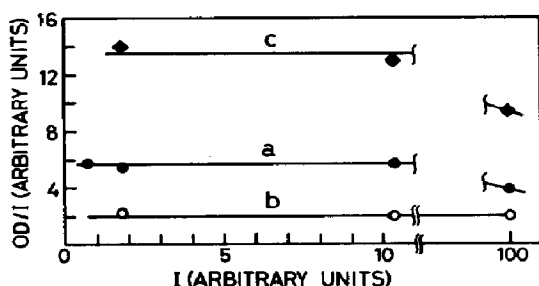

Fig. 4. The absorption of the photoproduct as a function of the laser pulse intensity I: curve a, at 430 nm; curve b, at 500 nm; curve c, at 600 nm. The concentration of Nitro-BIPS was 1.3×10^{-4} M.

highest intensity the optical densities of all three species are directly proportional to the pulse intensity, indicating that their relative yields are not changed. Only at their highest intensity do the yields of the first ($\lambda = 430$ nm) and third ($\lambda = 600$ nm) species decrease.

Figure 5 shows that the increase in optical density of A_nB (OD_{600}), relative to the optical density of AB (OD_{500}), is proportional to the square root of the concentration of spiropyran in solution. A comparison of the kinetic constants in solvents of various viscosities was made to estimate the role of molecular diffusion. In isopentane (viscosity 0.22 cP) the constants of decay and growth are the same as those in methylcyclohexane (1 cP). In hexadecane (3.3 cP) they are slightly smaller, approximately $(4 \pm 1) \times 10^6$ s^{-1}. We can conclude that, in this range of viscosities, diffusion does not markedly influence the observed processes.

In order to exclude bimolecular interactions of transients, experiments were also carried out in micellar solutions of CTAB and Triton. The concentrations of the surfactants (10^{-2} M CTAB and 2% Triton) and of Nitro-BIPS (5×10^{-5} M) were chosen so that each micelle was occupied by no more than one molecule A. This means that only unimolecular reactions can proceed.

In Fig. 6 the spectra of the photoproducts which are formed in Triton solutions after laser pulse excitation are shown (similar spectra were obtained
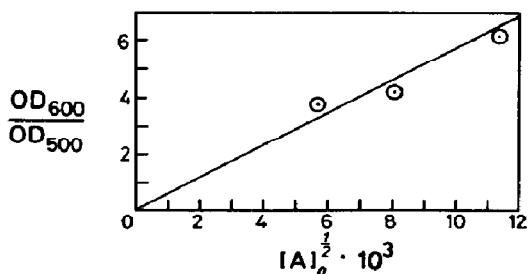
Fig. 5. The dependence of OD_{600}/OD_{500} on the concentration $[A]_0$ of Nitro-BIPS in methylcyclohexane.
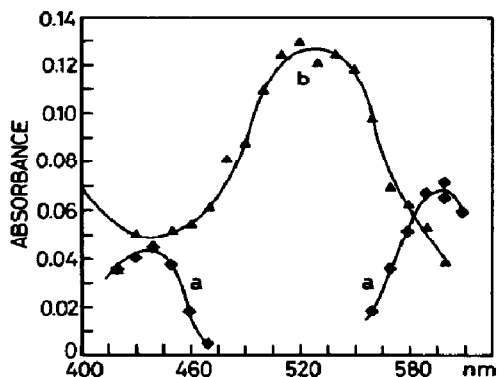
Fig. 6. The absorption observed after the laser flash for Nitro-BIPS solubilized in a water—Triton solution: curve a, difference spectrum of transients disappearing with $k = (4 \pm 1) \times 10^6$ s^{-1}; curve b, the spectrum of the long-lived product.

in CTAB solutions). The species having a maximum at 500 - 540 nm (curve b) is stable and its spectrum coincides with that of AB [3]. The two bands with maxima at 430 and 600 nm (curves a) disappear by first order kinetics with $k = (4 \pm 1) \times 10^6$ s^{-1}. These bands belong apparently to one transient, but in solutions of hydrocarbons only the band with $\lambda_{max} = 430$ nm was observed because of the very strong "permanent" absorption of the complexes A_nB above 560 nm. The stable band with $\lambda_{max} = 600$ nm observed in hydrocarbon solutions and assigned to the complexes A_nB does not appear at all. Thus we can conclude that these complexes are not formed under conditions where bimolecular interactions are excluded.

4. Discussion

From the experimental results it can be concluded that dimers AB are formed in a unimolecular reaction, probably by the phototransformation

$$AA \xrightarrow{h\nu} AB$$
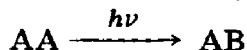
This implies that the equilibrium

$$2A \rightleftarrows A_2$$
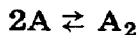
exists in solutions of Nitro-BIPS. Accordingly micelles may contain single molecules of either A or A_2. The dimers AB are stable and are not involved in any further transformation except for a slow back reaction

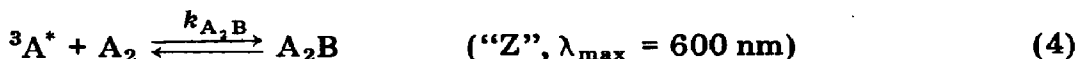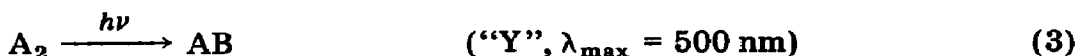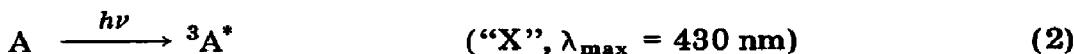$$AB \xrightarrow{\Delta} A_2$$
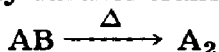
The results show that the complexes A_nB are formed from the transients "X" with the absorption maximum at 430 nm. A_nB can be formed in two ways — by unimolecular or by bimolecular reactions. In the first case

the following reaction scheme can be proposed. The association of spiropyran in solution goes further and the complexes A_3 or A_4 are formed. On irradiation A_nB ($\lambda_{max} = 600$ nm) is formed in addition to AB via an unstable precursor "X" ($\lambda_{max} = 430$ nm):

$$A_{n+1} \xrightarrow{\;h\nu\;} \text{"X"} \to A_nB$$
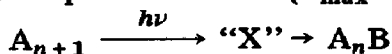
From this mechanism a marked dependence of the relative yields of AB and A_nB on the initial concentration of spiropyran is expected, contrary to the experimental results. The data obtained with the solubilized solutions of A are also in disagreement with this scheme, since no A_nB formation is observed under these conditions.

The second possible mechanism is a bimolecular scheme. We then assume that the transient "X" is the triplet spiropyran $^3A^*$, in agreement with results described previously [7, 8]. The much shorter lifetime measured by us could be ascribed to the oxygen quenching. The triplet molecules then interact with the A_2 dimers forming A_2B. The mechanism of this interaction awaits clarification, but the general scheme is as follows:

$$2A \rightleftharpoons A_2 \tag{1}$$

$$A \xrightarrow{\;h\nu\;} {}^3A^* \qquad (\text{"X"}, \lambda_{max} = 430\text{ nm}) \tag{2}$$

$$A_2 \xrightarrow{\;h\nu\;} AB \qquad (\text{"Y"}, \lambda_{max} = 500\text{ nm}) \tag{3}$$

$${}^3A^* + A_2 \xrightleftharpoons{k_{A_2B}} A_2B \qquad (\text{"Z"}, \lambda_{max} = 600\text{ nm}) \tag{4}$$

$${}^3A^* \xrightarrow{\;k_A\;} A \tag{5}$$

For solutions with small optical densities at 347.1 nm (the wavelength of the laser beam) the following is obtained:

$$[A_2] = K_{eq}[A]^2 \tag{6}$$

$$d[{}^3A^*]/dt = -k_A[{}^3A^*] - k_{A_2B}[{}^3A^*][A_2] \tag{7}$$

$$[{}^3A^*]_0 = I\phi_T\epsilon_A[A] \tag{8}$$

$$[AB] = I\phi_{AB}\epsilon_{A_2}[A_2] \tag{9}$$

$$d[A_2B]/dt = k_{A_2B}[A_2][{}^3A^*] \tag{10}$$

where I is the intensity of light in the laser pulse, K_{eq} is the equilibrium constant, ϕ_T and ϕ_{AB} are the quantum yields of $^3A^*$ and AB, ϵ_A and ϵ_{A_2} are the extinction coefficients of A and A_2 at 347.1 nm, k_{A_2B} and k_A are the rate constants of reactions (4) and (5), and $[^3A^*]_0$ is the initial concentration of $^3A^*$ produced by the laser pulse. Equations (7) and (10) give

$$[{}^3A^*] = [{}^3A^*]_0 \exp(-t/\tau) \tag{11}$$

$$[A_2B] = k_{A_2B}\tau[^3A^*]_0[A_2] \{1 - \exp(-t/\tau)\} \tag{12}$$

and, for $t \to \infty$

$$[A_2B]_{lim} = k_{A_2B}\tau[^3A^*]_0[A_2] \tag{13}$$

where τ $(=(k_A + k_{A_2B}[A_2])^{-1})$ is the lifetime of $^3A^*$. Our results show that τ does not depend markedly on the concentration and viscosity of the solution and, even in micellar solutions where reaction (4) does not take place at all, τ $(=(k_A)^{-1})$ is not changed significantly. This means that

$$k_A \gg k_{A_2B}[A_2] \tag{14}$$

This is as expected because, with $k_A \approx 5 \times 10^6$ s^{-1}, inequality (14) must be valid for $[A_2]$ below 10^{-4} M, even if $k_{A_2B} = 10^9$ M^{-1} s^{-1}, *i.e.* it is diffusion controlled.

The ratio between the concentrations of $[A_2B]_{lim}$ and AB is equal to the ratio between eqns. (13) and (9):

$$\frac{[A_2B]_{lim}}{[AB]} = \frac{\epsilon_{AB}}{\epsilon_{A_2B}} \frac{OD_{600}}{OD_{500}}$$

$$= \frac{k_{A_2B}\tau[^3A^*]_0[A_2]}{I\phi_{AB}\epsilon_{A_2}[A_2]} \tag{15}$$

Introducing eqns. (6) and (8), and keeping in mind that $[A] = [A]_0 - 2[A_2]$ $([A]_0$ is the initial concentration of spiropyran), we obtain

$$\frac{\epsilon_{AB}}{\epsilon_{A_2B}} \frac{OD_{600}}{OD_{500}} = \frac{[A_2B]_{lim}}{[AB]}$$

$$= \frac{\phi_T\epsilon_A}{\phi_{AB}\epsilon_{A_2}} \frac{2k_{A_2B}\tau[A]_0}{\{(1 + 8K_{eq}[A]_0)^{1/2} + 1\}} \tag{16}$$

For the two extreme cases the ratio OD_{600}/OD_{500} is proportional to either $[A]_0$ or $[A]_0^{1/2}$:

if $8K_{eq}[A]_0 \ll 1$ $\qquad\qquad OD_{600}/OD_{500} \propto [A]_0 \tag{17}$

if $8K_{eq}[A]_0 \gg 1$ $\qquad\qquad OD_{600}/OD_{500} \propto [A]_0^{1/2} \tag{18}$

Since the results are in accordance with eqn. (18), we conclude that $K_{eq} \gg 1/8[A]_0$. This means that a substantial fraction of spiropyran exists as dimers A_2 even at concentrations of about 10^{-5} M. According to eqn. (16) OD_{600}/OD_{500} should not depend on light intensity, as is indeed observed. A reason for the apparent decline of the quantum yield of the formation of $^3A^*$ and, therefore, of the relative concentration of A_2B at very high light intensities may be the triplet annihilation

$$^3A^* + {}^3A^* \to A + {}^1A^*$$
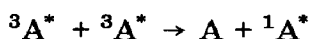
The results described in this work suggest that the composition of the polar complexes is A_2B rather than A_3B.

5. Conclusion

The results obtained in this work further the understanding of the mechanism of the early stages of formation of quasi-crystalline dispersions and quasi-crystals, preceding the phase transition and evolution of globules. It is clear now that the reactions for the formation of AB and A_nB are independent and do not compete directly. The increase in the relative concentration of AB on cooling may be caused by not only a change of k_{A_2B}, but also a shift in the equilibrium $2A \rightleftarrows A_2$ to the right. In accordance with the scheme, the increase of AB content in globules on continuous irradiation with intense light is caused by the relative decrease of the steady state concentration of $^3A^*$.

The existence of dimers A_2 in solutions of spiropyrans in aliphatic hydrocarbons is thus an essential condition for the production of quasi-crystalline material.

Acknowledgment

References

1 V. A. Krongauz and A. A. Parshutkin, *Photochem. Photobiol.*, *15* (1972) 503.
2 A. A. Parshutkin and V. A. Krongauz, *Mol. Photochem.*, *6* (1974) 437.
3 V. A. Krongauz and E. S. Goldburt, *Nature (London)*, *271* (N5640) (1978) 43.
4 V. A. Krongauz, S. N. Fishman and E. S. Goldburt, *J. Phys. Chem.*, *82* (1978) 2469.
5 V. A. Krongauz and E. S. Goldburt, *Chem. Phys. Lett.*, *60* (1979) 251.
6 V. A. Krongauz, *Isr. J. Chem.*, *18* (1979) 304.
7 T. Bercovici, R. Heiligman-Rim and E. Fischer, *Mol. Photochem.*, *1* (1969) 23.
8 M. Mosse and J. C. Metras, *J. Chim. Phys. Phys.-Chim. Biol.*, *64* (1967) 691.
9 C. F. Koelsch and W. R. Workman, *J. Am. Chem. Soc.*, *74* (1952) 6288.
10 G. Beck, J. Kiwi, D. Lindenan and W. Schnabel, *Eur. Polym. J.*, *10* (1974) 1069.