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Decomposition of Merocyanine Aggregates into Monomers in UV-Irradiated Spiropyran Solutions as Revealed in Anomalous Absorption Decay at the Merocyanine Monomer Band

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The aggregates which absorb near 700 nm, formed on the UV-irradiation of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] in some nonpolar solvents, were found to decompose into monomers, through the anomalous absorption decay at the merocyanine monomer band.

Spiropyrans are noted for their photochromic behavior.[1,2] Molecules in the colorless spiropyran form (A) are transformed into the colored merocyanine form (B) on UV irradiation. The merocyanine form decays back thermally to the original colorless form following first-order kinetics. Among many types of spiropirans, 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6-nitro BIPS) is known to give aggregates on UV irradiation in nonpolar solvents. Krongauz et al.[3-5] reported the formation of "quasicrystals", which are globules of 0.2 - 0.4 μm in diameter, and showed many peculiar optical and electrochemical behavior. Onai et al.[6] obtained aggregates of a much larger size (70 - 100 μm) which precipitate out of the solution, and discussed their molecular structure based on their resonance Raman spectra. In the aggregates, merocyanine conformers are coupled each other by coordination via the NO group in the aci-nitro structure. These aggregates contain colored merocyanine species. The colored merocyanine form survives over days in Onai's large aggregates. Such aggregates can be used, for example, as a long-time memory material. Before such aggregates precipitate, aggregates of smaller aggregation number must be formed in solution. Temporal behavior of such smaller aggregates in solution is very intriguing.

In the present study, we have found anomalous non-exponential decay behavior of absorbance at the merocyanine monomer band in certain conditions in which the aggregates absorbing near 700 nm (corresponding to the "charge-transfer complex" reported by Krongauz[3,4]) were present in the solution. This anomaly can be interpreted by partial decomposition of the aggregates into merocyanine monomers. Deaggregation of merocyanine aggregate is found for the first time.

6-Nitro BIPS (Tokyo Kasei), cyclohexane, heptane, carbon tetrachloride, m- and p-xylene (Nakarai Tesque) were used as received. UV irradiation was performed with an Ushio 150 W xenon lamp. Concentration and temperature were 1.0 x 10^{-3} M (1 M = 1 mol dm^{-3}) and 20 °C, respectively. The solution in a 10 mm x 10 mm quartz sample cell was kept in a thermostatted water bath before and after the irradiation and during measurements of absorption spectra. Absorption spectra and absorption decay were measured on a Hitachi 200-20 double beam spectrophotometer equipped with a thermostatted sample cell holder.

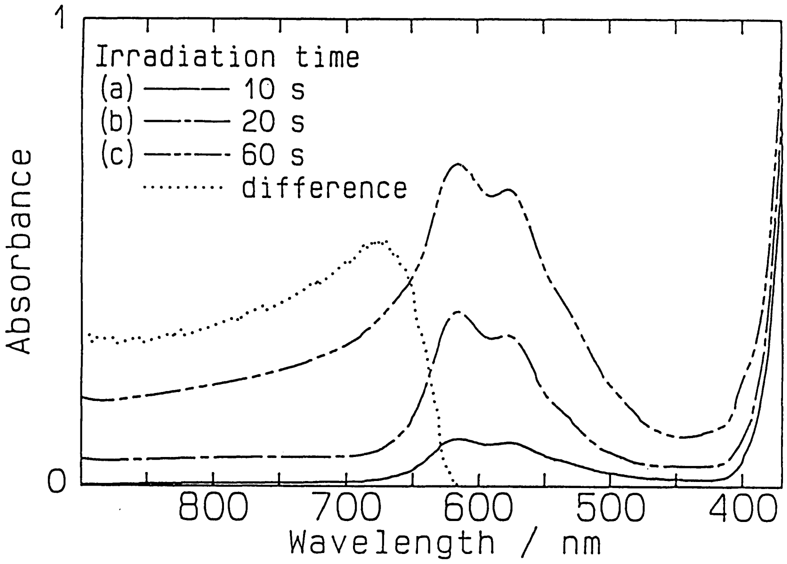

Fig. 1. Absorption spectra of a cyclohexane solution (1.0 x 10^{-3} M) of 6-nirto BIPS after UV irradiation for 10 (a), 30 (b), and 60 s (c). Temperature: 20 °C. Difference spectrum obtained from (c) and (a) is shown by the dotted line (in arbitrary units).

Absorption spectra of cyclohexane solution (1.0 x 10^{-3} M) after UV irradiation for 10 s, 30 s ,and 60 s are shown in Fig. 1. The bands at 580 nm and 620 nm are, respectively, attributed to the monomer (B) and dimer (AB) of the merocyanine form.[1,2]) The shoulder near 700 nm appeared on prolonged irradiation. A difference spectrum shown in the figure indicates the presence of a broad band at ≈700 nm. Krongauz et al. reported on the formation of an aggregate (charge-transfer complex, CTC, in their notation) with an absorption band at ≈700 nm in isopentane and methylcyclohexane solutions.[4,5]) The band must correspond to this "CTC".

Temporal variation of absorbance at 580 nm (corresponding to merocyanine monomer) is given in Fig. 2 (a) for 30 s irradiation. The measurement started at 20 s after irradiation was stopped. The initial part (≲ 40 s) of the decay deviated considerably from a single exponential behavior. This anomaly was less pronounced for 20 s irradiation, and not found for 10 s irradiation. Although photochromism of 6-nitro BIPS has been studied for a long time, such an anomalous decay behavior of merocyanine monomer band has not been reported to the best of our knowledge.

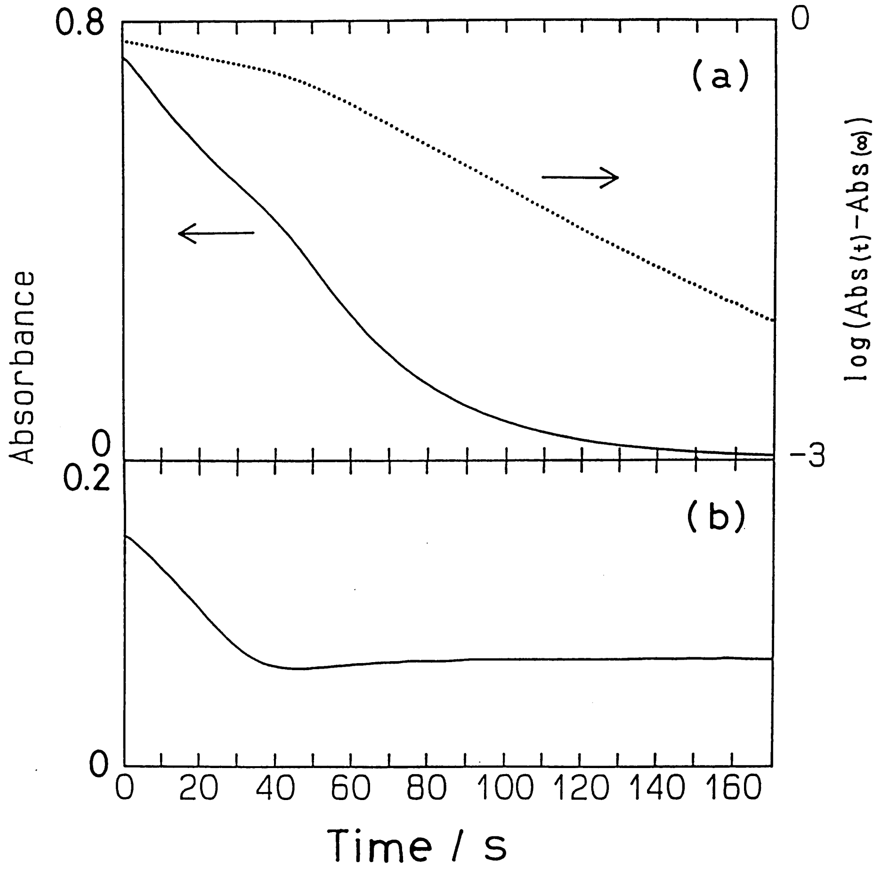

Fig. 2. Temporal variation of absorbance of the UV-irradiated (for 30 s) cyclohexane solution of 6-nitro BIPS (1.0×10^{-3} M). Measurement started at 20 s after irradiation was stopped. Temperature: 20 °C. (a) at 580 nm (merocyanine monomer band), (b) at 700 nm (shoulder due to the aggregate).

The anomalous decay behavior was found only for cyclohexane and heptane among the solvents used. Moreover, it was found to occur together with the occurrence of a shoulder near 700 nm. The absorbance at ≈ 700 nm decreased in the time domain of anomalous monomer decay ($\lesssim$ 40 s) as shown in Fig. 2 (b). The nonzero absorbance for the later time ($\gtrsim$ 40 s) shows that some portions of the aggregates remain for long time. The decomposition of the aggregates is only partial.

Apparently, the anomalous absorption decay in the initial time domain is due to the <u>increase</u> of merocyanine monomer (superimposed on its exponential decay) and this occurs concomitantly with the <u>decrease</u> of the aggregate which absorbs near 700 nm. Although Krongauz et al.[4,5] designated the aggregate absorbing near 700 nm (CTC in their notation) as A_nB, it is highly probable that more than two merocyanine units (B's) are contained in the aggregate, considering the fact that many merocyanine units are coupled in the larger aggregates found by Onai et al.[6] Therefore, we designate the aggregate absorbing near 700 nm as A_mB_n. Then the anomalous decay behavior can be interpreted by regeneration of B from the aggregate A_mB_n. The decay curve observed at monomer band can be considered as due to superposition of the main decay starting at t=-20 s (when UV irriadiation is stopped) and a convolution of additional decay curves which start between t=-20 and ≈40 s on the regeneration of the monomer.

The anomalous decay in the initial time domain was observed also for the dimer band at 620 nm (see Fig.3). This indicates that the regeneration of AB from A_mB_n also occurs.

Deaggregation of the aggregate as found in the present study, leading to regeneration of colored merocyanine, can be utilized as a means of elongation of the lifetime of colored merocyanine species.

In conclusion, the partial deaggregation of merocyanine aggregates (corresponding to CTC reported by Krongauz et al.) of 6-nitro BIPS back into merocyanine monomers and dimers was found by the observation of an anomalous absorption decay at the monomer and the dimer bands.

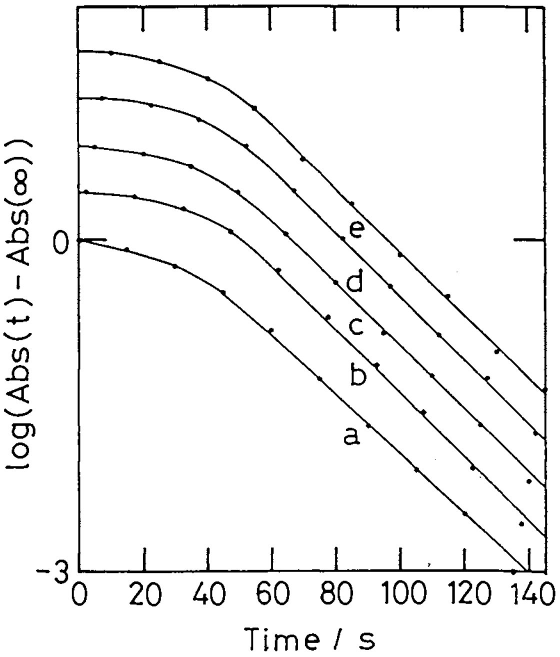

Fig. 3. Same as Fig. 2, except for the following. (a), (b), (c), (d), and (e): at 640, 620, 600, 580, and 560 nm, respectively. Absorbance values are read from the repeated scan of the spectra. Curves (b)-(e) are shifted upward for clarity. Temperature: 30 °C.

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