

Retardation of the Merocyanine-Spiropyran Conversion in Macromolecules

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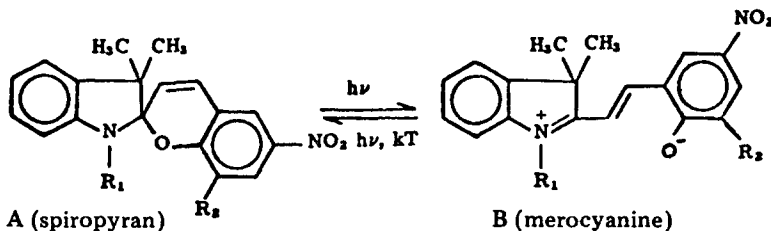
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SUMMARY

The flash photolysis of photochromic poly(spiropyranmethacrylate) in solutions was studied. The rates of the thermal decoloration reaction in the polymer solutions are lower than in solutions of the monomer, that was attributed to the steric hindrance of the reaction in macromolecules.

INTRODUCTION

Spiroyrans are among the most widely studied organic photochromes, they are converted reversibly into merocyanine dyes on irradiation with suitable light (BERTELSON 1971).



Photochromic polymers containing spiropyran moieties as side groups were obtained by copolymerization of vinyl monomers with spiropyrans containing polymerizable groups (VENDEVIJER, SMETS 1968, 1970; SMETS 1972; KARDASH et al. 1974). Comparison of the photochromic properties of the copolymers and the corresponding low molecular spiropyrans in solution showed that the quantum yields of the photocoloration do not differ appreciably but the rate of the ring-closing back reaction is substantially lower for the copolymers. This was ascribed to intramolecular interactions between the merocyanine and the comonomer side groups, resulting in stabilization of the merocyanine form.

It was found recently (LABSKY et al. 1980) that the reaction rate grows with the length of the side chain separating the photochrome from the main polymer chain. This was attributed to the higher frequency factor of the ring closing reaction in the polymer which has the longer hydrocarbon spacer in the side group.

A reversible viscosity decrease of photochromic polymer solutions by irradiation was also explained by similar intramolecular interactions, leading to shrinkage of the macromolecular coils (IRIE et al. 1979).

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The possibility of intramolecular interactions of the merocyanine groups with each other was not taken into account (VENDEVIJER, SMETS 1968; 1970) or even rejected (IRIE et al. 1979) though this possibility is quite feasible due to the bulkiness of these groups and the well known tendency of the merocyanines to undergo dipole-dipole interactions (STURMER, HESELTINE 1977; KRONGAUZ et al. 1978). Here we report the effect of such mutual interference of the merocyanine side groups of photochromic polymers on the thermal decoloration rate in solution.

RESULTS AND DISCUSSION

The flash photolysis apparatus described earlier (BERCOVICI et al. 1976) equipped with a Nicolet Digital Oscilloscope M206 was used. The solutions were bubbled with argon before irradiation to remove oxygen. The concentration of solutions was low (10^{-4} - 10^{-6} M in spiropyran monomer units) to obtain uniform absorption of the incident light. A four-fold decrease of the light intensity of the flash by a screen did not affect the initial optical density of the solutions after the flash, indicating that the intensity was sufficient to transform all photochromic side groups into the merocyanine form.

The atactic homopolymer poly(spiropyranmethacrylate) (PSMA) with $M_w \approx 3 \cdot 10^4$ was prepared by radical polymerization of the spiropyran with methacrylate substituent at indolyl nitrogen, i.e. $R_1 = -C_2H_4.OCO.C-(CH_3)=CH_2$ and $R_2=H$ (SMA) as described in (KRONGAUZ, GOLDBURT 1981).

The copolymers of SMA with methylmethacrylate (MMA) were prepared by a similar method.

The results of the flash photolysis for SMA, PSMA and copolymers SMA-MMA are summarized in Table I. The transients formed on irradiation of the polymers and the monomer have the same absorption spectra. The spectra coincide with those reported for the similar spiropyrans (BERTELSON 1971; KRONGAUZ et al. 1980) (a bathochromic shift of 20 nm was observed only for a SMA solution in benzene).

TABLE I: Half-life of the Merocyanine Form in Solution

Photochromic Materials	Solvent	λ_{max} (nm)	Half-life* (sec)
Monomer SMA	C ₆ H ₆	600	11
" "	MTHF	580	16
Copolymer SMA (4%)-MMA	C ₆ H ₆	580	35
" "	MTHF	580	40
Copolymer SMA (25%)-MMA	C ₆ H ₆	580	77
" "	MTHF	580	91
Homopolymer PSMA	C ₆ H ₆	580	350
" "	MTHF	580	130

*Average of five independent experiments; estimated uncertainty $\pm 10\%$.

Pronounced differences were observed for the rate of spontaneous decoloration of the solutions after the flash. The decay is exponential in all cases but the decay half-time is longer for the polymers than for SMA and grows with increasing spiropyran content in the polymer. For the homopolymer the half-life of the colored merocyanine moieties is about ten times longer than for the 4% copolymer. Varying the solution concentration (10^{-6} - 10^{-4} M) had no effect on the rate of decoloration. This is in agreement with the conclusion (VENDEVIJER, SMETS 1968, 1970; KRONGAUZ, GOLDBURT 1981) that the intermolecular interactions are of no importance in the polymer solutions.

Decoloration of the monomer and the copolymers proceeds more slowly in MTHF than in benzene. For the homopolymer the effect of the solvents is opposite.

The longer half-life of the monomer transients in MTHF may be ascribed to stabilization of the merocyanine form due to stronger solvation by the more polar solvent.

The slow rate of the copolymer decoloration is probably due to intramolecular solvation of the merocyanine groups by methacrylate ester groups (IRIE et al. 1979). This self-solvation presumably enhances the stability of the merocyanine form in the 4% copolymer. Effect of solvation of the merocyanines by the MTHF molecules, if any, lies within the experimental errors.

The distinct rise of the half-life of spontaneous decoloration with the increase of the fraction of SMA in copolymers from 4 to 25% indicates that interactions between merocyanine side groups become essential for decoloration of the polymer with the increasing spiropyran content. These interactions are likely to control decoloration of the homopolymer because it does not contain methylmethacrylate groups. The effect of the solvent polarity for PSMA is very pronounced, and opposite that observed for SMA.

We can consider two simple explanations of the retardation of the merocyanine Δ spiropyran reaction in the polymers with high content of the photochrome: the dipole-dipole interaction between merocyanine side groups, or steric hindrance caused by the adjacent bulky photochrome groups. The identity of the transient absorption spectra of the homopolymer and the copolymer with low content of SMA (where interactions between merocyanines must be negligible) apparently weighs against the first explanation. If the second one is correct, the lower decoloration rate of the homopolymer in benzene (than in MTHF) can be connected with the very low solubility of the polymer in C_6H_6 (less than 10^{-3} M). In such a bad solvent the molecular coil is probably very dense, and the reaction with the substantial change of geometry of the side groups must involve enhanced steric hindrances. We suppose that the time of the decoloration of the polymer characterizes the density of the macromolecular coils.

Further work in this direction is now in progress.

REFERENCES

- BERCOVICI, T., KORENSTEIN, R., FISCHER, G., and FISCHER, E.,
J. Phys. Chem. 80, 108 (1976)
- BERTELSON, R., Photochromism, Techniques of Chemistry, V.3 Ed.
G. Brown, Wiley Intersci., pp. 45-293 (1971)
- IRIE, M., MENJU, A., and HAYASHI, K., Macromol. 12, 1176 (1979)
- KARDASH, N.S., KRONGAUZ, V.A., ZAITSEVA, E.L., and MOVSHOVICH,
A.V., Polym. Sci. USSR 16A, 453 (1974)
- KRONGAUZ, V.A., FISHMAN, S.N., and GOLDBURT, E.S., J. Phys. Chem.
82, 2469 (1978)
- KRONGAUZ, V.A., KIWI, J., and GRATZEL, M., J. Photochem. 13, 89
(1980)
- KRONGAUZ, V.A. and GOLDBURT, E.S., Macromol. 14, 1382 (1981)
- SMETS, G., Pure Appl. Chem. 30, 1 (1972)
- STURMER, D.M. and HESELTINE, D.W., The Theory of Photographic
Process, Ed. Jammes, H., Macmillan, N.Y. (1977)
- VENDEVIJER, P.H. and SMETS, G., J. Polym. Sci., C22, 231 (1968);
8, A-1, 2361 (1970)

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