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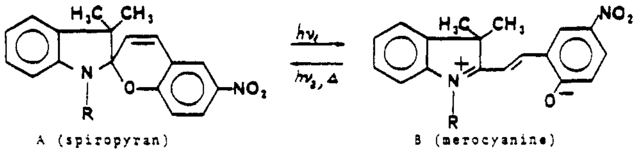
Communications to the Editor

A Simple Relationship between Rate of Color Change and Molecular Weight of a Photochromic Spiropyran Polymer

Kinetic studies of photochromic reactions of polymers containing the spiropyran side groups have been the subject of a number of publications.[1-5] However, little attention has been paid to the fact that the kinetics of the thermal merocyanine–spiropyran conversion can be complicated by the very strong tendency of the merocyanine molecules to form molecular stacks.[6-9] Our recent flash photolysis studies of dilute solutions of some polyvinyl macromolecules with pendant indolinobenzospiropyran groups revealed that decoloration of the homopolymers in such nonpolar solvents as benzene and toluene proceeds at a much slower rate than that of the monomers or copolymers with a low content of the spiropyran groups.[7] Decoloration of the copolymers and monomers fits first-order kinetics whereas the color decay of the homopolymers is described by a superposition of two exponential decays. The spectra of irradiated homopolymers in nonpolar solvents are also a superposition of two absorption bands that fade at different rates. This was ascribed to the presence of two types of merocyanines.[7] The first type, characterized by a shorter wavelength absorption band ($\lambda_{max} \simeq 560$ nm) and slower decay rate, was considered as the "stacked" merocyanine groups (the absorption maximum in this region is typical for so-called H-stacks[6,7]). The second type of merocyanines with $\lambda_{max} \simeq 580$ nm and faster color decay rate was considered as the "nonstacked" groups. Taking into account that the concentrations of the polymer solutions were very low (10^{-4}–10^{-5} M monomer units or 10^{-6}–10^{-7} M macromolecules) we assumed that *intra*molecular stacking occurs in loops or other closely spaced segments of the macromolecules. This implies that the probability of loop formation for such rigid macromolecules as poly(spiropyran methacrylate) (PSMA) with bulky merocyanine side groups should sharply decrease as the macromolecule size diminishes below a certain magnitude. In the present work we tested this idea by measuring the decoloration rate of irradiated PSMA in toluene solutions as a function of the molecular weight of the polymer.



Experimental Section. Spiropyran-substituted methacrylate monomer ($R_1 = (CH_2)_2OCO(CH_3)C{=}CH_2$) and corresponding homopolymer were prepared as described in ref 7 and 10. The weight-average molecular weights (M_w) of the polymers were determined by ultracentrifugation as in ref 6. Six molecular weight fractions were separated by fractional precipitation of the polymer solution in MTHF with methanol. M_w of the unfractionated polymer was 3.1×10^4. The crude molecular weight distribution of the unfractionated polymer is shown in Figure 2a.

The color decay measurements of the irradiated polymer solutions in toluene were carried out by flash photolysis as described in ref 7. The optical density change was monitored at the absorption maximum 560 nm. The absorption change at 580 and 550 nm showed the same decay rate. The high flash intensity provided a complete initial transformation of the spiropyran groups to merocyanine ones.

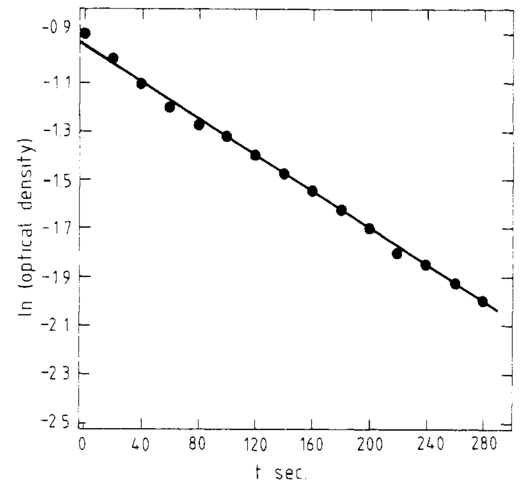


Figure 1. Kinetics of merocyanine–spiropyran conversion for the polymer with $M_w \simeq 5.3 \times 10^4$. The points are the experimental data. The line is based on the first-order kinetics.

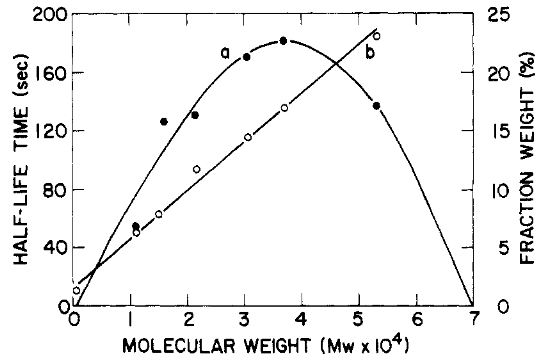


Figure 2. (a) Molecular weight distribution of unfractionated polymer. (b) Half-life time of merocyanine–spiropyran conversion vs. average molecular weight.

Results and Discussion. The color decay of the irradiated toluene solutions of each polymer fraction obeys the first-order kinetics (Figure 1). This is in contrast to the unfractionated polymer decoloration, which we could satisfactorily describe only by a two-exponential function.[7]

The half-life times ($\tau_{1/2}$) of the merocyanine–spiropyran conversion in the macromolecules are shown in Figure 2b as a function of the average molecular weight of the fractions. The function is linear and can be described by the equation

$$\tau_{1/2} = \ln 2/k = 3.2M_w + 10 \qquad (1)$$

or

$$k = 1/(2p + 14) \qquad (2)$$

where k is the first-order rate constant of the decay and p is the degree of polymerization. It is remarkable that the monomer decay time (M_w = 420, p = 1) fits well into the line extrapolated to M_w = 0.

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The simplicity of the function (2) allows us to make an important mechanistic conclusion: For $p \gg 7$, the decay rate depends inversely on the degree of polymerization. For example, if we "cut" each macromolecule in half there is a twofold increase in the rate of decoloration. The explanation is easy if we assume that (a) only the edge merocyanine groups in a stack are converted into spiropyrans (i.e., the conversion occurs step-by-step from the ends of the stacks) and (b) each macromolecule forms only one stack, whose length is proportional to the degree of polymerization. The last assumption is inconsistent with a simple idea on the stack formation in the macromolecular loops. Indeed, it is hard to imagine that a macromolecule would form only one stack, irrespective of macromolecular length. Formation of loops in short macromolecules is in particular hindered by the stiffness of the polymethacrylate backbone bearing the bulky spiropyran or merocyanine groups. On the other hand, the formation of the *intra*molecular stacks can be explained if one assumes that the macromolecules have a regular configuration such as a helix, which would allow the possibility of the merocyanine molecules to form the stacks with a periodic structure.

The alternative explanation is based on the assumption that the merocyanine stacks are formed by *inter*molecular association of the macromolecules. Tazuke and co-workers found efficient association of macromolecules by donor–acceptor interactions of the side groups in an extremely dilute solution. Corresponding low molecular compounds do not associate in solution (see ref 11 and references therein). The second explanation could account for the fact that polydisperse polymer merocyanine–spiropyran conversion is described by the two-exponential function whereas the fractionated polymer decays with first-order kinetics. The association of macromolecules of different lengths leaves part of the merocyanine groups "unstacked". These "unstacked" groups are converted to the spiropyran groups faster than the "stacked" ones. The portion of the "unstacked" groups must be much less for the associated macromolecules of an equal length and the merocyanine–spiropyran conversion fits the first-order kinetics well.

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Registry No. A (spiropyran) (R = $(CH_2)_2OCO(CH_3C{=}CH_2)$ (homopolymer), 99342-38-8.

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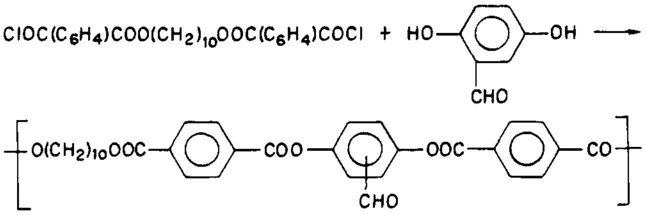
Transformation of a Monotropic Liquid Crystalline Polymer to an Enantiotropic One by Increasing Molecular Weight of the Polymer

There is an interesting phenomenon associated with liquid crystalline compounds: some are monotropic whereas most are enantiotropic. A compound is enantiotropic if it shows a stable liquid crystalline state both on heating to above its melting point (or, in certain instances, glass transition temperature) and on cooling from above its clearing temperature (i.e., isotropization temperature). It is monotropic, on the other hand, if it shows a liquid crystalline state only on cooling. It is believed that the monotropism is usually due to the extent of the crystalline order being great enough to preserve the true solid above the range of mesophase thermal stability,[1] and it is, therefore, possible to reveal the potential enantiotropic behavior of a monotropic compound by sufficiently depressing the melting point of the solid. For many low molecular weight systems various impurities have been used to achieve this objective.[2] A recent report from Lenz's group discussed the work of transforming an apparently non-liquid crystalline polymer to nematic by incorporating a small amount of a comonomer into the polymer chains.[3] Although copolymerization can depress a melting point and thus favor the formation of a liquid crystalline state, a polymeric system also can be changed significantly by the incorporation of comonomers. No matter how little the amount of added comonomer, the polymer behaves as a copolymer and not as a homopolymer. There are also monotropic systems of polymeric compounds. The transformation of a monotropic liquid crystalline compound to an enantiotropic one by increasing molecular weight was first observed by Blumstein and coworkers.[4] They synthesized model compounds of the nematic polyester poly(2,2′-dimethyl-4,4′-dioxyazoxybenzene-dodecanedioyl) and found that molecular weight and molecular weight distribution have a drastic influence on transition temperatures and mesophase stability. Their model compounds 9-DDA-9 and 9-DDA-9-DDA-9 are monotropic, and the lowest molecular weight to display an enantiotropic nematic phase is approximately 2800. Recently, we synthesized a monotropic liquid crystalline polyester of low molecular mass by polycondensation of 1,10-bis((chloroformyl)benzoyloxy)decane and 2-formyl-1,4-dihydroxybenzene.[5] In this communication we report the conversion of this monotropic polymer to an enantiotropic one by increasing polymer molecular weight.

Experimental Section. The polymer was synthesized by the solution polycondensation of the monomers 1,10-bis((chloroformyl)benzoyloxy)decane and 2-formyl-1,4-dihydroxybenzene:



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