

# Spiroprans and Spirooxazines for Memories and Switches

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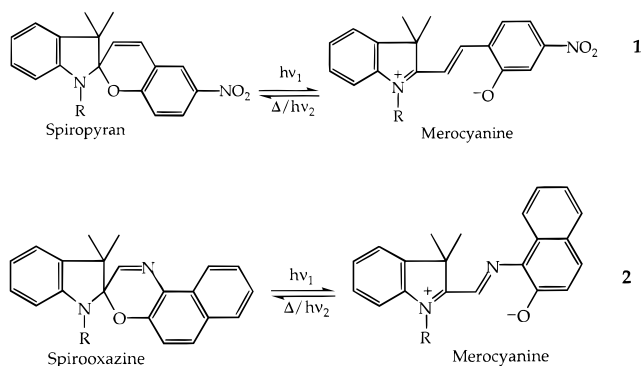
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## I. Introduction

Typical examples of photochromic reactions of spiropyrans **1** and the closely related spirooxazines **2** are the reversible photochemical cleavage of the C–O bond in the spiropryan or spirooxazine rings:



Comprehensive reviews on the photochromism of

spiropyrans and related compounds are given in books,<sup>1–6</sup> which covered the literature until 1990. More recent information on the topics is contained in the proceedings of the 1st and 2nd International Symposia on Organic Photochromism<sup>7,8</sup> and in a recent monograph.<sup>9</sup>

Discovery of the photochromic reactions of spiropyrans by Fischer and Hirshberg<sup>10</sup> in 1952 and Hirshberg's idea of using the phenomenon for a "photochemical erasable memory"<sup>11</sup> initiated active research on photochromism. Numerous other applications based on reversible color and other changes in physical and chemical properties were suggested and examined for photochromic spiropyrans and spirooxazines: self-developing photography, actinometry, displays, filters, and lenses of variable optical density, including eye-protective glasses, etc. The two most interesting directions were started recently: three-dimensional optical memory based on a two-photon-generated spiropyran–merocyanine conversion<sup>12</sup> and photoswitching of protein activity by a spiropyran covalently bound to the protein.<sup>13</sup> A detailed review on photoswitchable biochemicals was previously published by Willner<sup>14</sup> and is not addressed here.

In the present review, we consider three topics relating to potential applications of spiropyran–merocyanine systems in memories and switches. The first topic is the formation of organized structures, such as aggregates and mesophases whose optical properties, including nonlinear ones, can be affected by an electric field. The second topic is the nonlinear optical properties of the photochromic systems, and the third topic is real-time holography, employing photochromic spiropyran and spirooxazine systems.

## II. Organized Photochromic Materials

### A. Spiropyran–Merocyanine Aggregates

The colored merocyanine form of the photochrome has a very strong tendency to associate into aggregates with a stack-like arrangement of the mero-



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Valeri Krongauz was born in Russia in 1928. He received his M.Sc. degree in chemistry from the Moscow University, and his Ph.D. and Dr.Sc. degrees from the Karpov Physical-Chemistry Institute, where he continued researching energy transfer in radiation and photochemical reactions until the mid-1960s when he began studies on the kinetics and mechanism of organic photochromic reactions. He immigrated to Israel in 1976 and joined The Weizmann Institute of Science as a professor of chemistry. Numerous new photochromic materials have been synthesized and investigated during the past 30 years by Professor Krongauz, including photochromic polymers, photochromic liquid crystals, and liquid crystal polymers that are sensitive to light and to an electric field. In 1997 he became a professor emeritus of the institute, and is involved in the development and production of photochromic materials at Chromtech Co., Israel.

cyanine molecules.<sup>15</sup> When the molecular dipoles are arranged in a parallel (head-to-head) structure (the so-called J-aggregates), their absorption spectra are shifted to the red, as compared with the isolated merocyanine molecules. In the case of the antiparallel (head-to-tail) dipole arrangement (H-aggregates), the spectra are shifted to the blue. Under certain conditions, when a spiropyran solution is irradiated in a nonpolar solvent, the aggregates produce a very peculiar form of colloidal-sized beads with submi-



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rometer J-aggregate cores and an amorphous exterior. Under an external electrostatic field the beads form threads along the electric lines of force.<sup>16</sup>

The tendency for merocyanine aggregation is so strong that the aggregates are formed on irradiation of a spiropyran in a methacrylate polymer and even on swelling of the polymer film in a solvent.<sup>17</sup> Under prolonged irradiation in a more dilute spiropyran solution, rather stable three-dimensional J-type crystals (up to 100  $\mu\text{m}$ ) are formed.<sup>18</sup>

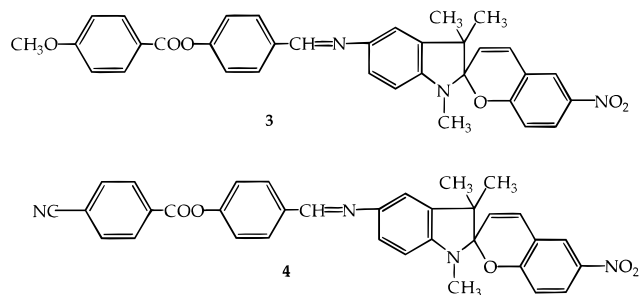
Particularly stable J-aggregated films were prepared by Hashida et al.<sup>19</sup> from spiropyrans with long hydrocarbon tails covalently connected to both the indoline and benzopyran parts of the photochromes. These compounds were used to prepare multilayered, J-aggregated, thin-layer films on glass surfaces. The aggregates had well-separated, sharp absorption maxima, which could be erased separately by irradiation with a pulsed dye laser beam of different frequencies. The device was suggested as a model for a multifrequency reversible optical memory cell.

## B. Photochromic Mesophases

### 1. Quasi-Liquid Crystals

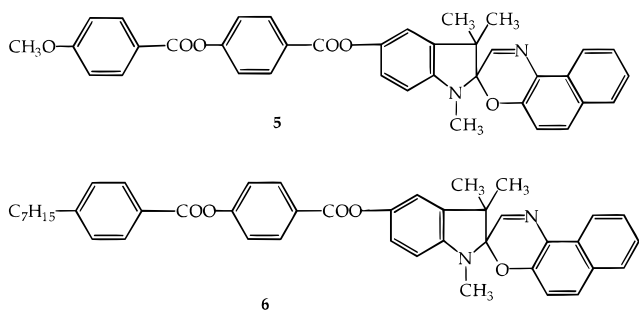
The main goal in preparing photochromic liquid crystals is to obtain a material responding reversibly to both an electric field and light. The most straightforward design of such a material would be a "hybrid" molecule composed of mesogenic and photochromic units.

Compounds **3** and **4** represent examples of such combined molecules.<sup>20</sup> These compounds form a metastable mesophase, which can be aligned in an electrostatic field and stabilized by supercooling to room temperature. In this respect the mesophase resembles a liquid crystal polymer below  $T_g$ . The molecules **3** and **4** are not photochromic, but concentration of the colored merocyanine molecules is substantial in the melt due to the thermochromic



effect. This leads to their aggregation and to the distortion of the liquid crystalline order, which in turn decreases the clearing temperature, sometimes below the crystal melting point. The materials were named quasi-liquid crystals (QLCs).

Molecules **5** and **6** represent QLCs that show the photochromic effect.<sup>21</sup> The supercooled films of these



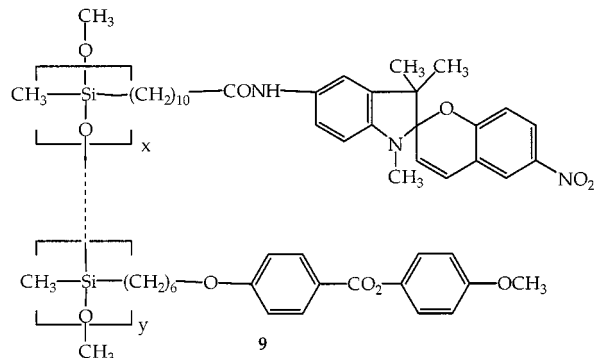
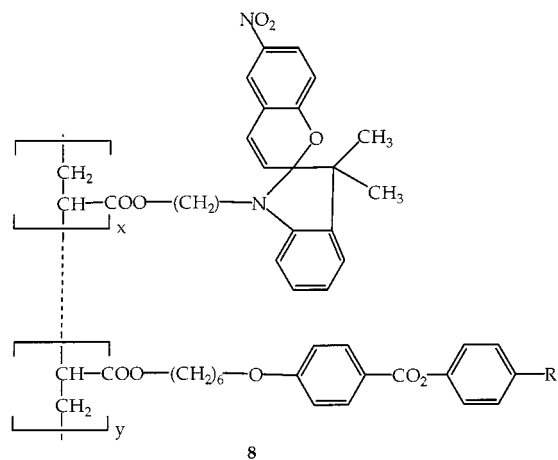
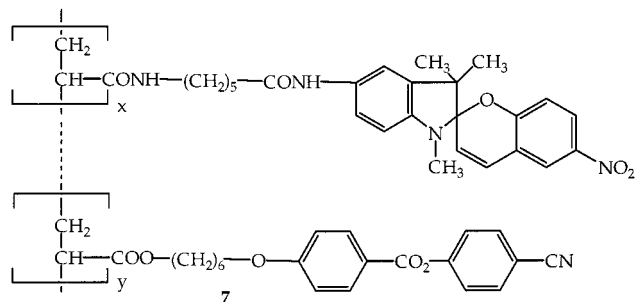
compounds form blue merocyanine molecules (non-aggregated) on UV irradiation, which are spontaneously converted back to a noncolored spirooxazine form in the dark.

Under an electrostatic field, both aggregated merocyanine molecules, which are "frozen" in the mesophase below  $T_g$ , and nonaggregated ones, which are formed on irradiation, are oriented along the mesophase alignment direction.

## 2. Photochromic Liquid Crystal Polymers (PLCPs)

While the combination of photochromic and mesogenic groups in one low molar mass molecule seldom gives photochromic liquid crystals, the synthesis of side-chain liquid crystal polymers containing both mesogenic and photochromic groups represents a much more universal approach for obtaining the photochromic mesophase.<sup>3c</sup> It opens many possibilities in molecular engineering because the mesogenic and photochromic groups are more autonomous in this case. For example, the relative content of the functional groups in a macromolecule, length of the flexible spacers, structure of the main chain, molecular weight, and many other characteristics of a polymer can be easily tailored. Examples of polyacrylic, polyamide, and polysiloxane photochromic side chain liquid crystal polymers are **7**, **8**, and **9**.<sup>22,23</sup>

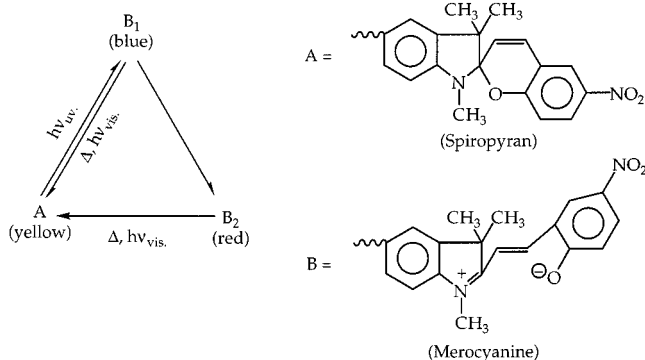
Phase transitions of PLCPs containing spiropyran side groups are influenced by thermochromic spiropyran-merocyanine side groups.<sup>23</sup> The spontaneous conversion of the associated merocyanine groups to spiropyrans on cooling the copolymer is insignificant, and the purple color, which belongs to the dimers acquired by the film on heating, is preserved after



cooling below  $T_g$ . The blue color, which is typical for nonaggregated merocyanine groups, fades on cooling.

Spectacular color transformations occur in polysiloxane copolymers.<sup>23</sup> The high flexibility of the chain segments, characteristic of polysiloxanes, leads to polymers with glass transitions below room temperature, which in turn affects the photochromic transformations in these polymers. The copolymer films cast from solution form a mesophase (strong birefringence) at room temperature. Irradiation with visible light brings about a pale-yellow color, while irradiation of the yellow film with UV light results in a deep-red color. A yellow film irradiated with UV light at  $-20^\circ\text{C}$  turns blue, and can be converted back to yellow by irradiation with visible light. The blue film is stable in the dark at  $-20^\circ\text{C}$  but turns red upon heating above  $-10^\circ\text{C}$ . The red film is thermally fairly stable but turns yellow on irradiation with visible light. At room temperature the fading of the red color takes several days or more, but less than 1 min above the clearing point. The purple-red color ( $\lambda_{\text{max}} = 550\text{ nm}$ ) corresponds to aggregated merocyanines, which cause physical cross-linking of the

Scheme 1



macromolecules. The blue color ( $\lambda_{\max} = 580$  nm) has been ascribed to isolated merocyanine groups. The yellow color ( $\lambda_{\max} = 370$  nm, tailing into the visible) corresponds to the spiropyran absorption. The induced color transformation can be explained by the mechanism given in Scheme 1.

The alignment of the photochromic liquid crystal copolymers in an electric field is quite similar to that of the corresponding nonphotochromic liquid crystal homopolymers. It is convenient to align a polymer homogeneously between parallel electrodes deposited on a glass slide to measure the order parameter of the dye units. An electrostatic field of about 1 kV/mm is usually sufficient to homogeneously align the liquid crystal polymer with the appropriate dielectric anisotropy at a temperature above  $T_g$ . Cooling the aligned films below  $T_g$  in the electric field and subsequent UV irradiation produce dichroic absorption in the visible, which allows estimation of the orientational order of the dye.

The orientation of photochromic as well as permanent dyes depends on the shape of the dyes and their means of fixation. For example, the merocyanine formed on irradiation of acrylic copolymers with spiropyran groups gives an order parameter of 0.1–0.2, while 4-dimethylamino-4'-nitrostilbene (DANS) dissolved in the same copolymers gives a substantially larger order parameter, 0.5, probably because of the better compatibility with mesogenic domains. The low order parameter for the merocyanine groups formed from spiropyran was explained by the assumption that the photochromic groups are accommodated outside mesogenic domains. This is also confirmed by the rather weak influence of the mesophase on decoloration kinetics and the absence of impact of photochromic conversion on the film alignment.

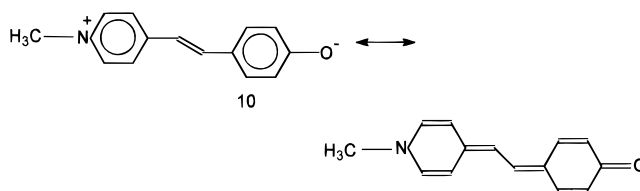
The hypothesis of the existence of two sites in photochromic side chain liquid crystal polymers (mesogenic domains and amorphous sites) implies that polymer backbones and photochromic side chains are located in the amorphous site, which is expanded with an increase of the photochrome content until the mesophase eventually vanishes. However, a certain "mixing" of mesogenic domains and spiropyran groups occurs, which is manifested in a non-zero-order parameter and certain retardation of thermal color decay in some copolymers.

### III. Nonlinear Optical Properties of Spiropyran–Merocyanine Systems

In organic molecules, nonlinear optical (NLO) properties are generally associated with conjugated  $\pi$  electron systems. Since such electronic structures are found in typical photochromic molecules, they can exhibit interesting nonlinear optical properties. In particular, the photochromic transition from spiropyran to merocyanine is accompanied by a major change in the conjugation of the  $\pi$  electrons, and thus large changes occur in the NLO properties. In this section we review many interesting NLO studies associated with the merocyanines, and the photochromic transformation between spiropyran and merocyanine. For a more detailed background into the molecular origins of optical nonlinearity and the various types of NLO phenomena—both second- and third-order—reviews which have been presented elsewhere are recommended,<sup>24,25</sup> as well as the review by Delaire and Nakatani in this issue.

#### A. Second-Order NLO Properties

Merocyanine dyes have some of the highest known molecular second-order NLO ( $\beta$ ) coefficients.<sup>26</sup> It has been shown<sup>24</sup> that, for typical organic NLO molecules,  $\beta$  is proportional to the oscillator strength of the transition to the lowest excited state, and to the difference in dipole moments ( $\Delta\mu$ ) between the ground and excited states. The large  $\beta$  values for merocyanine-type molecules can be understood<sup>26–30</sup> by considering its structure as an admixture of ionic and quinone resonance forms, as follows from its conjugated  $\pi$  electron system. This is represented<sup>26</sup> for the merocyanine molecule **10** as

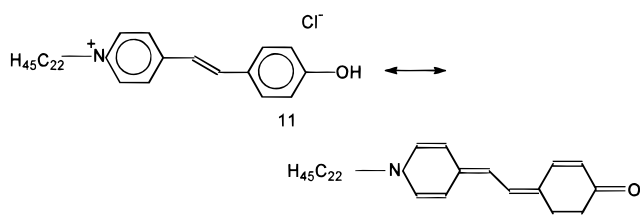


The ionic resonance form will have an extremely large dipole moment, which may reach 50 D, while the quinoid form has a much smaller dipole moment.<sup>26</sup> The true ground-state structure will be some admixture of these resonance forms; the weights of the contributions will determine the actual dipole moment. In a typical polar solvent, the zwitterionic form will contribute substantially, giving a resultant dipole moment of 26 D.<sup>27</sup> The dipole moments of the ground and excited states, and the difference between them,  $\Delta\mu$ , have been discussed<sup>28,29</sup> in terms of the "bond length alternation" (BLA) model. The admixture of the two resonance forms determines the length of a given chemical bond, and one examines the difference in lengths of adjacent bonds. BLA is greatest in the pure resonance forms, and reaches zero for 50% admixtures of the two forms. The actual contribution of each resonance form in a given merocyanine molecule—and thus  $\Delta\mu$ —can be solvent dependent, leading to a large solvent dependence on experimental  $\beta$  values.<sup>29</sup> Typically, for merocyanines

the dipole moment is larger in the ground state, leading to large negative  $\beta$  values.<sup>27</sup> The large negative  $\Delta\mu$  for merocyanine in common solvents also causes its well-known negative solvatochromism, i.e., a large blue shift in the absorption peak in solvents of increasing polarity.<sup>28,31</sup> Another manifestation of the relationship among molecular resonance structures, solvatochromism,  $\Delta\mu$ , and nonlinearity is presented by electroabsorption spectroscopy, also known as Stark spectroscopy.<sup>32</sup> The absorption spectrum of a merocyanine in solution will shift when the molecule is exposed to an external electric field. The applied field will change the internal electronic distribution in the molecule, analogous to the effect of changing the solvent.

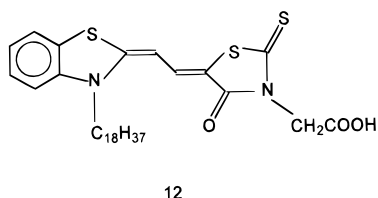
Other studies of second-order optical nonlinearity of merocyanines have used optical second harmonic generation (SHG) as a sensitive structural probe in noncentrosymmetric environments. As has already been described, irradiating spiropyrans under the influence of an external electrostatic field can produce colloidal globules and QLCs. SHG was used to deduce structural information about these unique structures.<sup>33,34</sup> SHG was observed from cooled QLC films, indicating that the merocyanines have a partial polar alignment along the direction of the electrostatic field used in their preparation. Subsequent application of an electric field to the QLC films amplified the signal, whereas application of a negative electric field (i.e., in the opposite direction) led to its cancellation. Further increase of the negative field strength achieved a realignment in the negative field direction.<sup>34</sup>

More detailed information about microscopic structure has been obtained from SHG studies of Langmuir–Blodgett (LB) films.<sup>35–38</sup> LB films of **11** were



analyzed by SHG, showing that the long axis of the molecule is essentially perpendicular to the glass substrate. For films transferred from a compressed monolayer, analysis of the SHG polarization ratios gave a value of  $9^\circ$  for the angle between the molecular long axis and the surface normal.<sup>35</sup>

Langmuir–Blodgett films have also been studied<sup>36–38</sup> for molecules such as **12**. The SHG signal



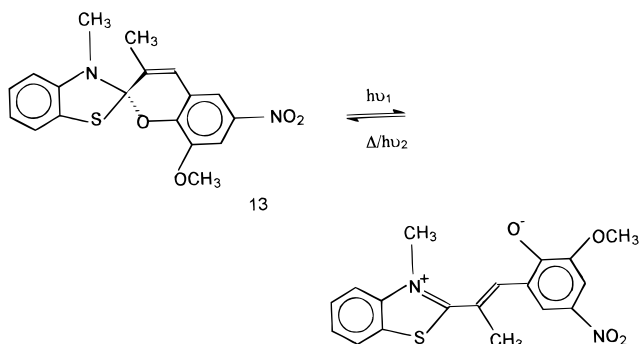
provided information about the structure of domains of J-aggregates, showing variations as a function of

deposition method, deposition pressure, and thermal treatment after deposition.

To observe SHG from NLO chromophores in polymers, the isotropic structure must be perturbed, and a common technique is the application of an electric field (poling) around the glass transition temperature,  $T_g$ , followed by cooling.<sup>24</sup> Several SHG studies, using the photochromic transformation between the nonconjugated spiropyran form (low  $\beta$ ) and the merocyanine (high  $\beta$ ) form, have been carried out in polymer matrixes, including derivatized polymers where the chromophore is covalently attached to the polymer. For example, a polypeptide has been derivatized with spiropyran and poled,<sup>39</sup> to give a material whose SHG efficiency is dependent on whether it is light sensitized or kept in the dark. Similarly, switching of the SHG intensity by irradiation has been reported for poled spiropyran in poly(methyl methacrylate) (PMMA).<sup>40</sup>

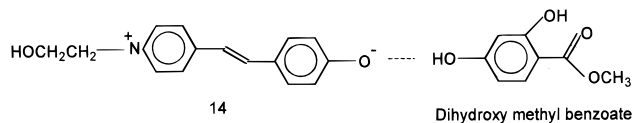
We have also demonstrated light-switchable modulation of SHG<sup>41</sup> in the spiropyran–merocyanine (SP–MC) containing quasi-liquid crystals (molecules **5** and **6**) and photochromic liquid crystal polymer **7** described in the previous section. However, a more remarkable effect first seen in this study was the creation of a stronger nonlinear response perpendicular to the applied field, rather than parallel to it. Although this phenomenon is not related to photochromism, the photochromic and aggregation properties of SP–MC helped prove that the perpendicular nonlinearity arose from an anisotropic distribution of charged dimers formed as a result of charge injection during the in-plane poling process.<sup>42</sup> By simultaneously monitoring absorption and SHG when the merocyanines decayed thermally to spiropyran, we observed a clear correspondence between the perpendicular nonlinearity and the merocyanine aggregate population. The weaker nonlinearity parallel to the field decayed similarly to the merocyanine monomer population.

An interesting variation of the usual  $T_g$  poling process—photoassisted poling (PAP)—uses light to enable poling at room temperature<sup>43</sup> as described in the review by Delaire and Nakatani in this issue. Two groups reported<sup>44,45</sup> photoassisted poling experiments on blends of spiropyran in PMMA. One group<sup>44</sup> studied SHG of molecule **13** in PMMA, while the other group<sup>45</sup> probed the changes in second-order nonlinearity by the electrooptic effect.



Another means to achieve large second-order nonlinearities in a bulk medium is in noncentrosymmet-

ric crystals. To the best of our knowledge, no photochromic spiroopyran or merocyanine is known to crystallize in a noncentrosymmetric crystal. However, production of noncentrosymmetric merocyanine cocrystals with large SHG has been reported<sup>46–49</sup> when merocyanine was cocrystallized with a second component, creating a hydrogen-bonded network. For example, in one such study<sup>46</sup> merocyanine **14** in a 1:1



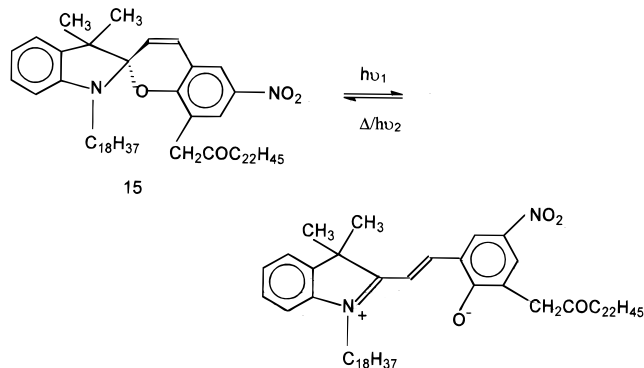
mole ratio with dihydroxymethyl benzoate was shown to give noncentrosymmetric crystals on the basis of the hydrogen-bonded packing motif shown. Two different noncentrosymmetric crystal phases were found, both exhibited promising second-order NLO coefficients for SHG and electrooptic modulation.

Merocyanine molecules have also been incorporated into a photorefractive polymer composite containing a photoconducting polymer, plasticizer, and sensitizer as well as the NLO chromophore.<sup>50</sup> Merocyanine was used as the NLO chromophore, and the performance of this composite was compared to that of composites containing an azo dye known to give a strong photorefractive effect. Photorefractive efficiencies were quite similar, and an improvement of about a factor of 5 was achieved for an optimized mixture of the azo and merocyanine dyes. This improvement was ascribed both to higher NLO efficiency for the merocyanine and to a decrease of merocyanine aggregation in the presence of the azo dye.<sup>50</sup>

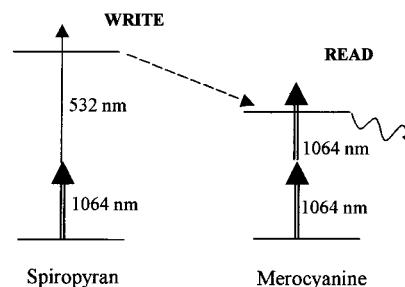
## B. Third-Order NLO Properties

Merocyanines also have large third-order nonlinearities, and we will review the results of several studies, performed in both the transparent and absorption regimes. Strong optical third harmonic generation (THG)<sup>51</sup> and an intensity-dependent refractive index<sup>52</sup> have been observed from merocyanine microcrystals.

In another study,<sup>53</sup> the photochromic transformation from spiroopyran to merocyanine caused a large light-switchable change in the third-order nonlinearity, in the same way as the second-order nonlinearity.<sup>53</sup> The authors chose molecule **15** since the mero-



cyanine form of some spiroopyrans substituted with



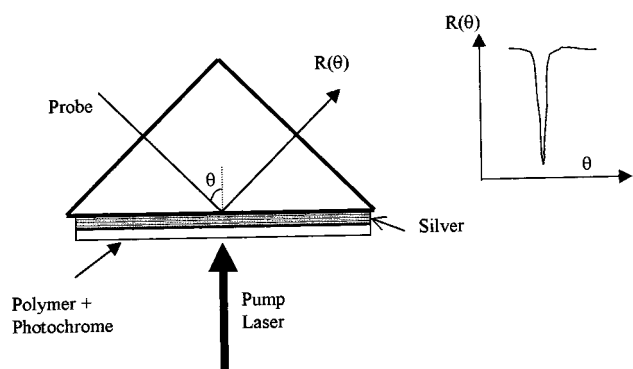
**Figure 1.** Scheme for three-dimensional optical recording based on photochromism of spiroopyran (from ref 54). Information is written by a two-photon absorption (532 nm + 1064 nm) of spiroopyran, which leads to merocyanine formation in the volume element where absorption occurred. Reading of information is absorption of two 1064 nm photons, followed by fluorescence.

two long-chain alkyl groups gives much more stable J-aggregates.<sup>53</sup> Films (1:1) of the spiroopyran form of **15** in a PMMA matrix were irradiated by UV light to produce merocyanine; aging at 30 °C for 12 h produced the J-aggregates as evidenced by a shift in the merocyanine absorption peak from 580 to 600 nm with considerable narrowing of the peak. THG of these films was probed by tunable laser light in the region 1.5–2.1  $\mu\text{m}$ ; the maximum THG was recorded around 1.8  $\mu\text{m}$ , corresponding to a three-photon resonance with the J-aggregate absorption. The THG of irradiated films was 50 times stronger than that of unexposed films. The J-aggregated regions of the films were stable for more than a year at room temperature, but could be reversibly transformed back to spiroopyran by heating to 80 °C.

Two-photon absorption (TPA) in a photochromic system was suggested as an efficient means for “three-dimensional” data recording.<sup>54</sup> Using tightly focused lasers, TPA will only occur in the small volume element defined by the focus; thus, a given volume element (pixel) in the medium can be addressed selectively by appropriate translation along three axes (for a linear absorption process, only two-dimensional recording is possible). The process can be envisaged as shown in Figure 1, and uses a spiroopyran molecule whose merocyanine form is fluorescent.

Simultaneous absorption of one photon from a (strong) 1064 nm laser beam and a second photon from a (weaker) 532 nm beam mutually focused on a certain pixel will “write” information by creating merocyanine in that pixel. This information can be read by monitoring fluorescence emission following irradiation using only the focused 1064 nm laser, as now only the merocyanine can be excited by two-photon absorption of this laser. Recorded information can be erased locally by irradiation, or entirely erased by heating. This principle was first suggested in 1989<sup>54</sup> and subsequently developed in more detail.<sup>12,55</sup>

More interest has been directed to resonant third-order NLO effects, where the absorption or refractive index of the sample becomes dependent on the light intensity. Under these circumstances, one may observe saturable absorption, optical limiting, spatial light modulation, the optical Kerr effect, and optical bistability. All these effects arise due to the creation



**Figure 2.** Surface plasmon geometry of ref 58 for demonstration of ultrafast switching of the probe beam following the spiropyran–merocyanine transformation.

of molecules in an excited or photoproduct state with different absorption characteristics. Photochromic materials will generally afford these effects over longer time scales—and thus build up a larger nonlinear response—than regular, nonphotochromic species, where a short-lived excited state perturbs the absorption. Photochromic fulgides were used in early studies of saturable absorption and bistability.<sup>56,57</sup>

The spiropyran–merocyanine transformation has been used to demonstrate ultrafast switching resulting from the change in refractive index.<sup>58</sup> In this study, a right-angle prism is covered on its hypotenuse with a thin film (50 nm) of silver, and a film of spiropyran in polystyrene. A He–Ne probe beam will be strongly reflected (as shown in Figure 2), except at a certain well-defined angle of incidence, at which light will be coupled into the silver film. Small changes in the refractive index of the polymer film will cause a measurable change in this angle.

Irradiation as shown with a 355 nm pump initiates the photochromic conversion of spiropyran in the polymer to merocyanine. This causes a small change in the refractive index, and consequently the angle at which the reflectivity dips due to the surface plasmon resonance. Ultrafast switching of light in (or out) of the plasmon resonance was demonstrated; the refractive index change was registered by the probe beam within 20 ns of the pump beam. The merocyanine state was thermally stable for at least 30 s, but could also be rapidly photoconverted back using a 600 nm laser; again the refractive index changes were observed within 20 ns.

#### IV. Photochromic Materials for Real-Time Holography

Several organic and inorganic photochromic media were investigated in the past as recording materials for holography.<sup>59–63</sup> The reader is also referred to general reviews on materials for in situ and real-time optical holographic recording, all of which have some advantages, but also some limitations.<sup>64–71</sup> A very important advantage of photochromic materials lies in the fact that they need no chemical or physical development, so they can be exploited for in situ optical recording.<sup>1–3,72</sup> Moreover, the recorded information can either be permanently stored or be erased for repeated recordings. For example, due to their

photochromic nature, the recording layers may first be recorded by coloration with UV radiation and then erased by bleaching with visible light or by heat, or vice versa.

Some basic characteristics of photochromics are important for holographic recording and storage, including exposure sensitivity, diffraction efficiency, and thermal (dark storage) and environmental stability. The exposure sensitivity of photochromic systems depends on the photochemical and thermal reaction kinetics, which in turn depend on the spectral absorption cross-section, quantum yield, wavelength of excitation, temperature, concentration, and solvent of the photochromic compound.<sup>1–3,73</sup> Unfortunately, one of the limitations of photochromic recording materials was their low exposure sensitivities to visible recording irradiations, typically over 1 J/cm<sup>2</sup>, so that they were not practical for real-time applications. With UV laser holographic recording, the exposure sensitivities were usually higher (0.1–1 J/cm<sup>2</sup>),<sup>62,74,75</sup> due to the fact that photochromic quantum yields are usually significantly higher in the UV region than in the visible. However, new investigations on real-time holographic recording in photochromic spirooxazine- and spiropyran-doped polymer thin films revealed that the exposure sensitivity in the visible could be significantly increased by choosing the proper optical recording procedure.<sup>76,77</sup>

Another limiting parameter with real-time holographic recording involving spiro compounds is their low diffraction efficiencies (DEs), usually not exceeding a few percent. This limitation is mainly due to the absorptive characteristics of the colored merocyanine, yielding lossy amplitude holograms, when read with probing beams of wavelengths falling within their absorption band. Increased DEs of over 10% were found for holograms recorded by UV laser beams in spiropyran-doped polymers, when probed at the absorption minimum at 488 nm.<sup>75</sup>

Below, we first consider in some detail erasable organic photochromic polymer materials incorporating spiro dyes for real-time and in situ holographic recording, to determine what factors influence exposure sensitivities and diffraction efficiencies.<sup>75–79</sup> Specifically, it is shown how the temporal holographic response and exposure sensitivity of such photochromic doped polymers are influenced by optical recording procedures. Photokinetic modeling indicates that the effects originate from optical addressing of different photochromic stereoisomers.<sup>77,78</sup> We also show the possibility of modulating holographically recorded gratings by modulating an external UV excitation beam.<sup>76</sup>

Photochromic materials were also considered with respect to optical recording with middle infrared (IR) laser radiation.<sup>80–82</sup> In the near-IR, spirothiopyran-doped polymer layers have been investigated for holographic recording by photobleaching of the colored dye with diode laser beams at 780 nm.<sup>78</sup> This was possible because the merocyanine absorption band of this spirothiopyran extends to over 800 nm. Yet, at wavelengths longer than about 1 μm, the exposure sensitivity of recording materials usually drops very rapidly, because the absorption of radia-

tion does not cause a change in the electronic levels, which could, in turn, induce primary photochemical reactions. Therefore, suitable materials that can record at long wavelengths in the infrared (IR) are very scarce.<sup>83,84</sup> Also, few real-time materials are available that possess suitable resolution capabilities in the middle IR. An alternative approach for recording in the IR may be accomplished with thermally activated reactions. Chemical bond dissociation or association is thermally activated through vibrational excitation. For example, the conversion of spiro-*pyran* to merocyanine (coloring and the back-conversion—bleaching—of merocyanine to spiro-*pyran*) is known to be both photochromic and thermochromic.<sup>1,2</sup> Therefore, the absorption of thermal radiation should, in principle, leave a permanent optical record in such systems. In this review, we consider recording IR irradiation by thermal bleaching in colored spiro-*pyrans*.<sup>81,82</sup> In these investigations, nonthermal processes at 10.5 and 10.6  $\mu\text{m}$  are also discussed.<sup>81,82</sup>

### A. Mechanism of Real-Time Holographic Recording with Visible Light

To explain the temporal holographic recording in photochromic materials, a semiempirical approach may be applied, describing a closed system of one independent rate equation. It was also assumed that a pseudo-first-order process with linear intensity dependence adequately describes the present photochromic system. These are reasonable assumptions, because, first, relatively low optical densities are involved ( $\text{OD} < 1$ ) and, second, low light powers are applied, so that nonlinear effects from multiphoton absorption can be neglected. Furthermore, in solid polymers, the thermal conversion from the colorless spiro compound **A** to its colored form **B** may be neglected. **B** may be a mixture of several stereoisomers<sup>1–3,85–88</sup> of the merocyanine form and their aggregates.<sup>3,89</sup> The overall change in concentration of **B** with time can then simply be given by the following rate equation:

$$-dB/dt = R_{\text{B}}B - R_{\text{A}}A + R_{\text{T}}B = R_{\text{B}}B - R_{\text{A}}A_0 + R_{\text{A}}B + R_{\text{T}}B \quad (1)$$

where  $A$  and  $B$  are the concentrations of the colorless and colored forms,  $R_{\text{A}}$  and  $R_{\text{B}}$  are the photochemical rate constants for the colorless and colored forms, and  $R_{\text{T}}$  is the thermal rate constant of conversion of **B** to **A**.  $A_0$  is the total concentration of all the dye species, satisfying  $A_0 = A(t) + B(t)$ . Integration of eq 1 with respect to  $B$  and  $t$  yields a general solution given by<sup>77,78</sup>

$$B(t) = (C_1/C_2)\{1 - \exp(-C_2t)[1 - (C_1/C_2)B(0)]\} \quad (2)$$

where  $C_1 = R_{\text{A}}A_0$ ,  $C_2 = R_{\text{A}} + R_{\text{B}} + R_{\text{T}}$ , and  $B(0)$  is the concentration of **B** at  $t = 0$ . Equation 2 represents the time dependency of  $B$ , exposed simultaneously to all photochemical and thermal processes, as indi-

cated in eq 1. The photochemical processes are characterized by their respective rate constants, which for species  $i$  is given by

$$R_i = I_i F_i \epsilon_i \phi_i (\lambda_i / Nhc) \quad (3)$$

where  $I_i$  is the light intensity ( $\text{J cm}^{-2} \text{s}^{-1}$ ) at wavelength  $\lambda_i$ ,  $F_i$  is a photokinetic factor, which corrects for absorption,  $\epsilon_i$  is the decadic molar absorption coefficient [or cross-section ( $\text{cm}^2/\text{mol}$ )],  $\phi_i$  is the quantum yield,  $N$  is Avogadro's number,  $h$  is Planck's constant, and  $c$  is the speed of light. For some exposure configurations, not all the processes will be active ( $I_i, F_i = 0$ ), and eq 2 can be simplified. The photokinetic factor in eq 3 is usually not a constant, as the absorbance is time dependent. However, here its time dependency can be either neglected or corrected for by normalization.<sup>78,79</sup>

When **B** is exposed to an interference pattern between two plane waves at  $\lambda_{\text{B}}$ , a cosinusoidal spatial modulation of concentration in the  $x$ -direction,  $B(x)$ , will be formed and thereby recorded as the holographic grating. Temporal holographic recording will therefore consist of a time-dependent spatial modulation,  $B(x, t)$ , as

$$B(x, t) = B_0(t) + B_1(t) \cos(2\pi x/d) \quad (4)$$

where  $B_0(t)$  and  $B_1(t)$  are the average and the peak of the (time-dependent) spatial modulation in concentration ( $\text{mol}/\text{cm}^3$ ), respectively, and  $d$  is the grating period. The gratings are recorded in the photochromic materials as a spatial modulation in absorbance. The time-dependent modulation is thus

$$a(x, t) = 2.303 \epsilon_{\text{B}} B(x, t) \quad (5)$$

where  $\epsilon_{\text{B}}$  is the absorption coefficient at the readout wavelength. The readout radiation can in principle also lead to photochemical interactions. To minimize destructive readout, the readout powers have to be significantly lower than those of the recording beams. The temporal diffraction efficiency  $\text{DE}(t)$  for thick amplitude gratings in photochromic materials<sup>90</sup> is

$$\text{DE}(t) = \exp(-2a_0(t)L/\cos \theta) \sinh^2(a_1(t)L/2 \cos \theta) \quad (6)$$

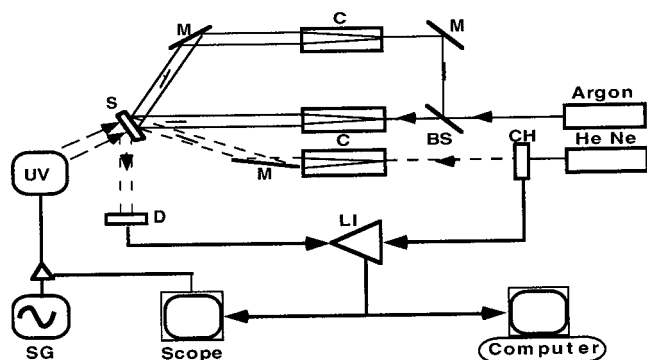
where  $a_0(t)$  is the (time-dependent) average absorbance,  $a_1(t)$  the amplitude of the absorbance modulation,  $L$  the grating thickness, and  $\theta$  the readout angle.

### B. Experimental Investigations

The photochromic polymer material systems which were investigated involved *spiro-*pyran** or *spirooxazine* derivatives blended at 5–10 wt % into PMMA or into poly(vinylcarbazole) (PVK) plastic binders, and coated as thin layers of thickness ranging between several micrometers and several tens of micrometers.<sup>74–76,79</sup>

A typical optics setup for recording and readout of simple holographic gratings is schematically shown in Figure 3. For experimental analysis, three different recording procedures were used.<sup>76,77</sup> In procedure a, the photochromic layers were initially exposed to a homogeneous and incoherent excitation beam from

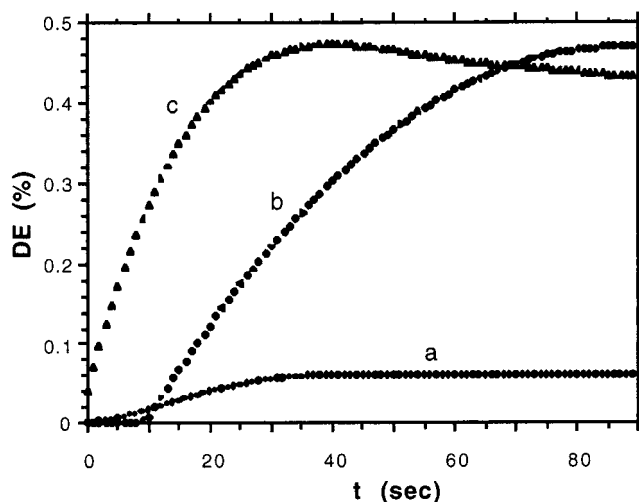




**Figure 3.** Schematic of the optics setup for holographic recording and readout. SG = signal generator, UV = mercury lamp, D = Si photodetector, S = sample, M = mirror, C = collimators and spatial light filters, BS = beam splitter, and CH = chopper.

a UV lamp at  $\lambda_A = 364$  nm, until maximal coloring occurred. The initial exposure was then followed by a simultaneous exposure to the two coherent Ar ion laser recording beams at  $\lambda_B = 514$  nm and to the UV excitation beam. At this stage of the exposure, the holographic interference pattern, created by the two coherent beams, is recorded by the bleaching of the colored merocyanine molecules, while, at the same time, new merocyanines are being formed by the homogeneous UV beam. In procedure b, the photochromic layers were again initially exposed to the UV excitation beam, until maximal coloring occurred. The initial exposure was then followed by a separate exposure to the two coherent Ar recording beams. At this stage of the exposure, the holographic interference pattern, created by the two coherent beams, is recorded by bleaching of the colored merocyanines only. Finally, in procedure c, the photochromic layer was first simultaneously exposed to the homogeneous UV excitation beam and to the two coherent recording beams. This was immediately followed by an additional exposure to the two recording beams only. At this stage of the exposure, the initially recorded holographic grating is enhanced by a further bleaching of the colored merocyanines.

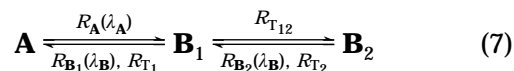
The results with the spirooxazine-containing samples are presented in Figure 4, showing the diffraction efficiency (DE) versus exposure time (holographic growth). These results were measured in real time by a He–Ne laser beam at 633 nm, operated at sufficiently low power ( $0.5$  mW/cm<sup>2</sup>) to minimize destructive readout. As is evident, significantly different holographic growth rates and exposure sensitivities are obtained for the three recording procedures. With the most sensitive procedure (c), the exposure sensitivity, i.e., the exposure needed for maximum DE, was found to be  $350$  mJ/cm<sup>2</sup> for the spirooxazine-doped layers. With the spiropyran-doped layers the corresponding exposure sensitivity was  $750$  mJ/cm<sup>2</sup>. These results therefore clearly indicate that the exposure sensitivities of a given photochromic material can be significantly increased (by a factor of about 2) by a variation in the optical recording procedure. These visible exposure sensitivities are within the same order of magnitude com-



**Figure 4.** Real-time DE versus exposure time ( $t$ ) of holographic gratings recorded at 514 nm in spirooxazine–PMMA films for three recording procedures (a, b, and c). Readout was at 633 nm. (a) Initial exposure to the UV (364 nm) excitation beam of  $5$  mW/cm<sup>2</sup> and then simultaneous exposure to the UV beam and to the two recording beams of  $9$  mW/cm<sup>2</sup>. (b) Initial exposure to the UV beam and then separately to the two recording beams. (c) Initial simultaneous exposure to all the beams, followed by exposure to the two recording beams only.

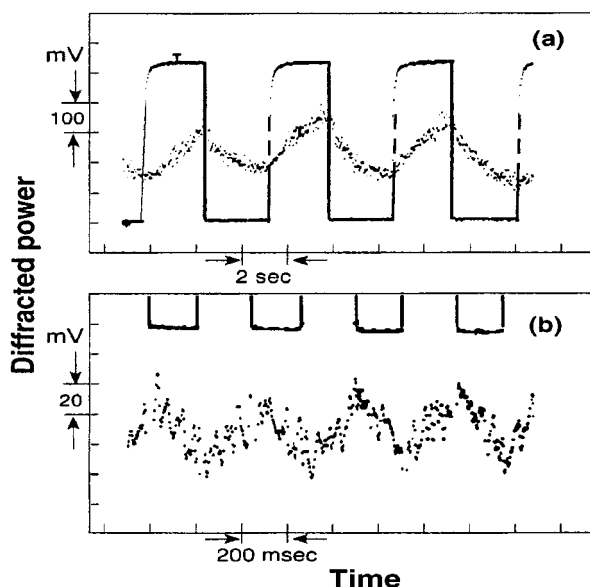
pared to those obtained for holographic recording in the UV.

The experimental results of Figure 4 can be explained by using eqs 2, 3, 5, and 6, and the proper boundary conditions for each of the recording procedures.<sup>77,78</sup> Specifically, the photokinetic rate constants  $R_B$  increased from about  $0.06$  s<sup>-1</sup> in procedures a and b, to about  $0.10$  s<sup>-1</sup> in procedure c. The corresponding quantum yields  $\phi_B$ , which were calculated according to eq 3, increased from about  $0.09$  to  $0.16$  einstein/mol. The existence of two thermal and photochemical decoloration rate constants indicates that a more suitable reaction scheme to explain the results of Figure 4 may be given by



where  $\mathbf{B}_1$  and  $\mathbf{B}_2$  are now two different forms of the colored merocyanine molecules, satisfying the relation  $\mathbf{B} = \mathbf{B}_1 + \mathbf{B}_2$ ,  $R_{B_1}$  and  $R_{B_2}$  or  $R_{T_1}$  and  $R_{T_2}$  are the respective photochemical or thermal rate constants for the transformations from  $\mathbf{B}_1$  to  $\mathbf{A}$  and from  $\mathbf{B}_2$  to  $\mathbf{B}_1$ , and  $R_{T_{12}}$  is the thermal rate constant for the transformation from  $\mathbf{B}_1$  to  $\mathbf{B}_2$ . The reaction scheme in eq 7 suggests a consecutive conversion among  $\mathbf{A}$ ,  $\mathbf{B}_1$ , and  $\mathbf{B}_2$ . However, a parallel conversion among  $\mathbf{A}$  and the two merocyanine forms may also be considered. The exact identities of the two merocyanine forms  $\mathbf{B}_1$  and  $\mathbf{B}_2$  cannot be derived from these holographic investigations, but they are most probably merocyanine stereoisomers of different thermal and photochemical stabilities.<sup>2,3,88</sup>

The experimental results of Figure 4 can now be interpreted in terms of the relative populations of the two merocyanine isomers  $\mathbf{B}_1$  and  $\mathbf{B}_2$ . With recording procedures a and b, the photochromic film is initially



**Figure 5.** Modulation of holographic gratings (dotted traces) as a result of square wave modulation of the UV beam (line traces). The modulated gratings were continuously exposed to the recording beams, each of  $20 \text{ mW/cm}^2$ : (a) with a modulation frequency of  $0.2 \text{ Hz}$ ; (b) with a modulation frequency of  $2.5 \text{ Hz}$ .

exposed to the UV excitation beam alone, so that at steady state the more stable colored isomers  $\mathbf{B}_2$  will be dominantly populated. A subsequent exposure to the visible recording beams causes decoloration to  $\mathbf{A}$ , with the rate-determining step being the transformation from  $\mathbf{B}_2$  to  $\mathbf{B}_1$  (and/or  $\mathbf{B}_2$  to  $\mathbf{A}$  in a parallel scheme). With recording procedure c, however, the initial exposure to all beams yields a mixture of all the species associated with the scheme of eq 7, with a significant population of  $\mathbf{B}_1$ . Therefore, a subsequent exposure to the recording beams causes decoloration at a significantly increased rate, being mainly determined by the transformation from  $\mathbf{B}_1$  to  $\mathbf{A}$ .

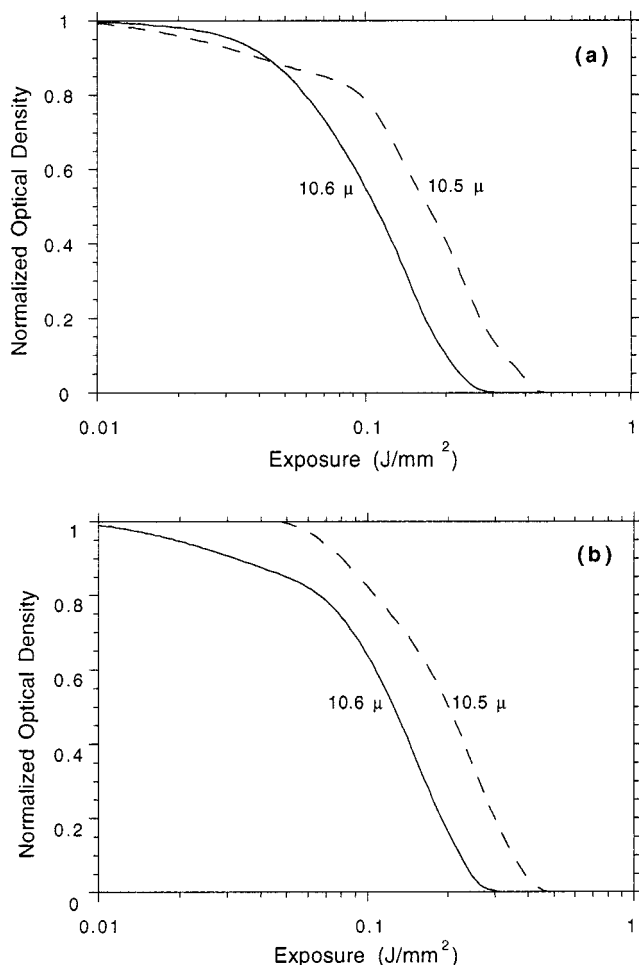
In a further step, when the layers are again simultaneously exposed to the UV and the recording beams, the DE is significantly reduced, since the UV beam partially erases the gratings. These results indicate that it should be possible to reversibly control the population of the photochromic isomers by optical addressing using the different recording procedures. Therefore, by modulating the UV excitation beam, it was possible to correspondingly modulate the holographically recorded gratings.<sup>76,79</sup> Figure 5 shows the results, when the gratings were continuously exposed to the recording beams, each of  $20 \text{ mW/cm}^2$ , while the UV excitation beam was modulated. The modulated UV excitation square waves are also shown in the figure. It was found that the photochromic layers doped with spirooxazine could be modulated at higher frequencies than the layers with spirocyan, as expected from their holographic exposure sensitivities. In addition, the temporal holographic growth rates and the modulation frequencies increased, when the recording beam intensities were increased, in accordance with our model predictions.<sup>77,78</sup> Similar increases in the temporal holographic growth and the modulation frequencies were obtained by increasing the excitation beam intensity.

Alternative holographic recording procedures were applied by Ghailane et al. in their experimental studies on spirocyan–poly(vinylcarbazole) blends.<sup>75</sup> Specifically, the UV line of a krypton ion laser was used for the recording, an Ar ion laser at  $488 \text{ nm}$  for readout, and a He–Ne laser for erasure. Variations in the layer thickness or the recording beam powers significantly affected both the exposure sensitivities and the diffraction efficiencies (DE). For example, at optimum conditions, a DE of over 10% was achieved at an exposure of about  $300 \text{ mJ/cm}^2$  in a  $12 \mu\text{m}$  thick layer. However, in layers of  $50 \mu\text{m}$  the DE dropped by more than 1 order of magnitude. The relatively high achievable DEs at optimum conditions may be attributed to the fact that at the readout wavelength there is negligible absorption. Therefore, a refractive index modulated phase grating is probed mainly,<sup>90</sup> as can be explained by using the Kramers–Kronig relation.<sup>79,91</sup>

### C. Recording in the IR

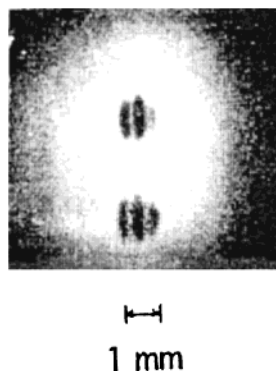
The feasibility of exploiting spirocyans for holographic recording at infrared wavelengths was first demonstrated by Izawa et al.<sup>80</sup> In their experiments, the spirocyans were blended with PMMA or polystyrene polymers. In more recent investigations, spirocyan–PMMA copolymers of increased thermal stability were used.<sup>81,82</sup> Specifically, the photochromic layers were first colored by irradiation from a UV lamp at  $364 \text{ nm}$  and an exposure energy of  $1 \text{ J/cm}^2$ . The colored photochromic samples were then incorporated into an optical setup, very similar to that depicted in Figure 3. However, in these experiments, a  $\text{CO}_2$  laser, rather than an Ar laser, was used. The samples were simultaneously illuminated with one or two recording beams at  $10.6$  or  $10.5 \mu\text{m}$  from the  $\text{CO}_2$  laser, and with a readout beam at  $633 \text{ nm}$  from a He–Ne laser. The change in optical density as a function of absorbed exposure to the  $10.6$  and  $10.5 \mu\text{m}$  lines of a  $\text{CO}_2$  laser are shown in Figure 6. The IR response is of the positive type; i.e., the optical density (OD) measured at  $633 \text{ nm}$  decreases as a function of the IR exposure. In other words, the laser radiation bleached the precolored merocyanine, thereby converting it back to spirocyan. It can be seen that there is a significant reduction in exposure sensitivity for the samples exposed at  $10.5 \mu\text{m}$ , when compared to those exposed at  $10.6 \mu\text{m}$ . Specifically, at 50% of the initial optical density, the exposure sensitivity was about  $0.1 \text{ J/mm}^2$  at  $10.6 \mu\text{m}$  wavelength and about  $0.2 \text{ J/mm}^2$  at  $10.5 \mu\text{m}$ .

It should be noted that the irradiations at  $10.6$  and  $10.5 \mu\text{m}$  are absorbed in these spirocyan-containing layers to different degrees, as indicated by IR spectroscopic data. Specifically, a strong band at  $\sim 959 \text{ cm}^{-1}$  ( $\sim 10.43 \mu\text{m}$ ) was assigned to the nitrogen–spirocarbon–oxygen (N–C–O) stretch vibration.<sup>92</sup> Therefore, the  $10.6 \mu\text{m}$  ( $\sim 941 \text{ cm}^{-1}$ ) laser line falls just outside that spiroband, whereas the  $10.5 \mu\text{m}$  ( $\sim 954 \text{ cm}^{-1}$ ) laser line falls well within that band. The results of Figure 6 indicate that the absorbed IR energy is dissipated by a different mechanism at each of these two wavelengths. When thin organic layers are on top of a thick glass substrate, which



**Figure 6.** Normalized optical density as a function of absorbed IR exposure energy of spiropyran-MMA copolymer layers. The irradiation wavelengths were 10.6 and 10.5  $\mu\text{m}$  from a  $\text{CO}_2$  laser. (a) The spiropyran concentration is 6 mol %. (b) The spiropyran concentration is 25 mol %.

represents a very efficient heat sink, small differences in thermal dissipation processes within the thin layers can be neglected. Therefore, the results in Figure 6, in conjunction with the spectroscopic data,<sup>81,82,92</sup> suggest that, since the 10.5  $\mu\text{m}$  radiation is essentially absorbed by the spiropyran molecules (because the  $-\text{N}-\text{C}-\text{O}-$  group does not exist in merocyanine), the thermal bleaching is retarded at 10.5  $\mu\text{m}$  because of partial spiropyran to merocyanine reversion (coloration). Such reversion may be neglected at 10.6  $\mu\text{m}$ , where the IR absorbance of the  $-\text{N}-\text{C}-\text{O}-$  group is much weaker. In other words, "hot" spiropyran molecules formed on absorption of 10.5  $\mu\text{m}$  radiation are reconverted to merocyanine before the absorbed energy is dissipated into heat. It must be noted that, with organic solids, it is extremely difficult to measure differences in vibrational excitation and relaxation processes, because the intermolecular energy dissipation is normally dominant. Nevertheless, such wavelength-selective IR laser induced chemical reactions were observed in the gas phase.<sup>93</sup> Finally, the results of Figure 6 also reveal that the exposure sensitivities are essentially independent of spiropyran concentrations; this indicates that the intermolecular merocyanine interactions and/or the degree of aggregate formation



**Figure 7.** Interference patterns of two beams from a  $\text{CO}_2$  laser, recorded in a photochromic polymer film.

do not play a significant role within the concentration range that we considered.

In related experiments, the interference patterns of two planar beams derived from a  $\text{CO}_2$  laser were recorded in the photochromic films. A photograph of a representative recorded interference pattern is shown in Figure 7. The distance between adjacent fringes was about 500  $\mu\text{m}$ . Also recorded were focused  $\text{CO}_2$  laser spots of about 25  $\mu\text{m}$  diameter, indicating that the resolution capabilities of these photochromic materials is equal or better than 40 lines/mm.<sup>80-82</sup> This resolution is similar to that reported with chemically developed silver halide materials that were used for recording 10.6  $\mu\text{m}$  radiation.<sup>94</sup>

In conclusion, it was shown that organic polymer layers, doped with photochromic spiropyran and spiropyran dyes, can be exploited for in situ and real-time holographic recording with visible laser light. Furthermore, all-optical modulation of the holographically recorded gratings was achieved by modulating a UV excitation beam. It was found that the temporal holographic growth is significantly influenced by the specific UV excitation and visible recording beam procedures. Specifically, the exposure sensitivities and modulation frequencies could be increased by changing the optical recording procedure and/or by increasing the UV excitation and visible recording beam powers. In these experiments, the maximal excitation and recording beam powers were limited, so that the holographic growth rates and the modulation frequencies were limited to about  $0.5 \text{ s}^{-1}$  and about 5 Hz, respectively. However, these can still be further improved by resorting to light sources of increased powers. The holographic results can be modeled by thermal and photochemical transformations between colorless spiropyran and at least two stereoisomeric forms of colored merocyanine. In other recording procedures, holographic recording in spiropyran-doped polymers was performed with UV laser beams and probed with visible Ar laser beams at an absorption minimum of 488 nm, and erased at 633 nm. These procedures yielded relatively high exposure sensitivities (several hundreds of  $\text{mJ}/\text{cm}^2$ ) and diffraction efficiencies (over 10%), and exhibited significant dependencies on coating thickness and recording beam powers.

Precolored photochromic spiropyran copolymers were also exploited for optical recording in the infrared. The results indicate that the recording is

predominantly due to thermal bleaching. However, as revealed by changes in exposure sensitivity with a small change in the CO<sub>2</sub> laser wavelength (from 10.5 to 10.6 μm), some nonthermal IR processes can also contribute during the recording. In related experiments, the interference pattern and focused spots derived from a CO<sub>2</sub> laser were recorded; the resolution capabilities were found to be over 40 lines/mm.

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