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Photoreversible optical nonlinearities of polymeric films containing spiropyran with long alkyl chains

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It was demonstrated that the third-order optical nonlinearity of polymer films could be reversibly controlled by the photochromic conversion and following *J*-aggregate formation of spiropyran embedded in an inert polymer matrix. Patterns consisting of areas with high and low third-order nonlinear optical activities were prepared by imagewise exposure of the photochromic films followed by thermal treatment to form thermally stable *J* aggregates of photoinduced merocyanine in the exposed area. This system could be useful in developing new unconventional optical devices based on optical nonlinearities, including new types of spatial light modulators. © *1996 American Institute of Physics.* [S0003-6951(96)03135-X]

Due to their potential applications for optical communications, data storage, and electrooptical signal processing, nonlinear optical (NLO) materials have been extensively investigated.[1] It is of particular interest to control the optical nonlinearity over a wide range with reversibility and repeatability, as would be necessary in the construction of spatial light modulators. A number of different types of electrooptic materials or general saturable and reverse saturable absorbers has been used as candidates for spatial light modulators; however, spatial resolution, electrooptic coefficients, and the cycle of time of the device or rate at which it can transfer images are not satisfactory.

It has been generally recognized that large π-conjugated dye show high NLO susceptibility.[2] Therefore photochromic compounds, whose structures can be reversibly changed between a noncolored form and a dye form by the stimulus of light, should be an important material for new types of spatial light modulators. Dantsker and Speiser have theoretically examined the utilization of photoreversible optical nonlinearities in trans-*cis* photochromic molecules for spatial light modulation.[3] One of the problems in the application of photochromic compounds to spatial light modulators is that the change of the optical characteristics caused by the structural change is not large enough between the noncolored form and the dye form. Another problem is that either the noncolored form or the dye form is not thermally stable enough to use it for some kinds of spatial light modulators.

Spiropyran is one of the typical photochromic compounds whose dye form, namely, merocyanine, is thermally unstable in nonpolar media. It has been reported, however, that the merocyanine form of some spiropyrans with two long alkyl chains forms thermally stable aggregates in Langmuir–Blodget films or bilayers.[4,5] One of the authors has discovered that the merocyanine molecules aggregate to form *J* aggregates even in some polymer matrices.[6] Here we report the effect of photochemical conversion from spiropyran into the *J* aggregate of merocyanine on the third-order NLO efficiency.

The spiropyran derivative used in this study (SP1822)[4] has the structure shown in Fig. 1. Two long alkyl chains on the spiropyran main frame stabilize the *J*-aggregate conformation. Thin films were prepared by spin coating of the mixture of SP1822, poly (methyl methacrylate) (MW=120 000 or 12 000) and chloroform onto a fused silica glass substrate. The weight ratio of SP1822 and the matrix polymers were 1:1. The film thicknesses measured by a Tencor Alpha-step 300 step height profiler were around 500 nm. The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in the wavelength range 200–900 nm. The third-order nonlinear optical properties were estimated by third-harmonic generation (THG). THG measurements were carried out between 1.5 and 2.1 μm of the fundamental wavelength, which was generated by mixing beams from a *Q*-switched Nd:YAG laser and a tunable dye laser using a LiNbO$_3$ crystal (Spectra Physics, DCR-10). The pulse width was approximately 5 ns, and the repetition rate was 10 Hz. The incident energy and the spot size on a sample were roughly 2 mJ per pulse and 2 mm^2, respectively. The observed THG was analyzed by the Maker fringe method. The apparatus was automatically controlled by a personal computer. Values of $\chi^{(3)}$ were determined by fitting to the follow-
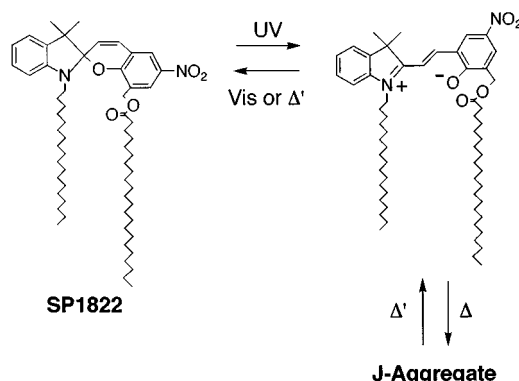

FIG. 1. Chemical structure of spiropyran with long alkyl chains (SP1822) and its isomerization reaction.

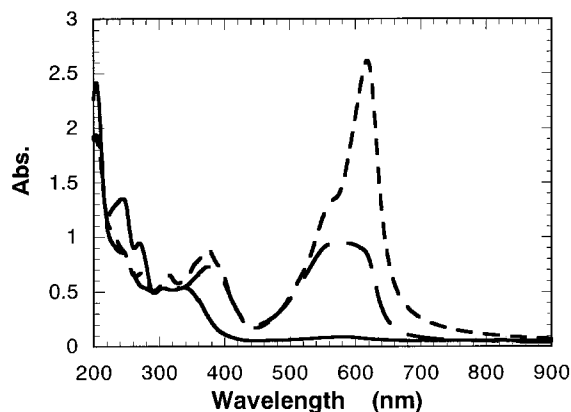[a]Electronic mail: ntamaoki@ccmail.nimc.go.jp

FIG. 2. Absorption spectra of poly (methyl methacrylate) (MW=120 000) film containing SP1822. Before exposure to UV light (solid line); after exposure to UV light (long-dashed line); after aging at 30 °C followed by exposure to UV light (short-dashed line).
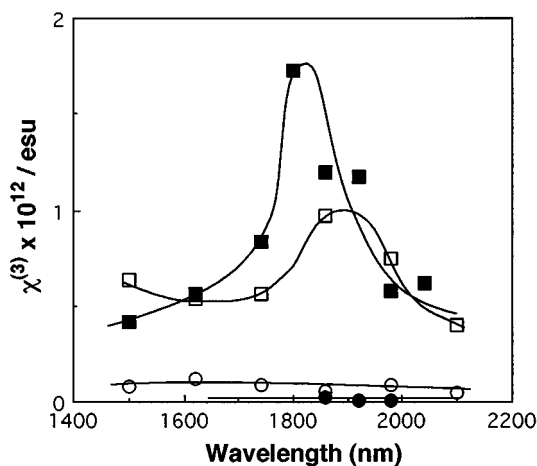

FIG. 3. Third-order nonlinear optical susceptibility of poly (methyl methacrylate) (MW=120 000 or 12 000) film containing SP1822. Before exposure to UV light (open circles) and after aging at 30 °C followed by exposure to UV light (open square) for poly (methyl methacrylate) (MW=12 000) film. Before exposure to UV light (closed circle) and after aging at 30 °C followed by exposure to UV light (closed square) for poly (methyl methacrylate) (MW=12 000) film.

ing equation.[7] A reference value $\chi^{(3)}=1\times10^{-14}$(esu) was used for fused quartz glass at all fundamental wavelengths.[8]

Equation for the determination of $\chi^{(3)}$ is

$$I_{3\omega}=\left| T_1 \frac{|\chi_s^{(3)}|}{\Delta\epsilon_s} e^{-i\Delta\psi_s/2} \sin(\Delta\psi_s/2) + T_2 \frac{|\chi_f^{(3)}|e^{-i\phi}}{\Delta\epsilon_f} e^{-i\Delta\psi_f/2} \sin(\Delta\psi_f/2) \right|^2 I_\omega^3,$$

where ϕ is the phase of $\chi^{(3)}$ of the film, $\Delta\epsilon=\epsilon(\omega)-\epsilon(3\omega) = n_\omega^2 - n_{3\omega}^2$, $\Delta\psi=6\pi t/\lambda_\omega(n_\omega \cos\theta_\omega - n_{3\omega} \cos\theta_{3\omega})$ is the phase mismatch between the waves at ω and 3ω in the medium, $n_{\omega,3\omega}$ is the refractive index, t is the film thickness, $\theta_{\omega,3\omega}$ is the angle of the wave inside the material makes with the normal, $T_{1,2}$ are transmission factors depending on the boundary conditions, and f and s refer to the film and substrate, respectively.

A transparent film obtained after coating was exposed to 366 nm ultraviolet (UV) light from a high-pressure Hg lamp (Ushio UI-501C) through an appropriate combination of glass filters (Corning color filters, 7-51 and 0-52). After exposure, the color of the film changed from transparent to violet and a new absorption band appeared at 580 nm. The violet film was placed in a drying oven maintained at 30 °C for 12 h (aging process). The absorption band of the aged film redshifted from 580 to 620 nm and became sharp and intense, which is the typical feature of the transformation from molecularly dispersed dye to J aggregate (Fig. 2).[4] The J aggregate was stable for more than one year under visible light at room temperature. No decrease of the absorption intensity nor any appearance of inhomogeneities, which includes crystallization of the spiropyran derivative, were observed.

The $\chi^{(3)}$ values of the unexposed film and aged film after exposing to 366 nm light are plotted against the fundamental wavelength in Fig. 3. The exposed film showed large third-order optical nonlinearity with three photon resonance to the absorption band of the J aggregates; the resonance $\chi^{(3)}$ values were on the order of 10^{-12} esu. On the other hand, the optical nonlinearity of unexposed film was small. The $\chi^{(3)}$ values of the unexposed film were 10–50 times

smaller than the exposed film depending on the polymer matrix. No optical damage of the film after the aging process was observed under the conditions of the THG measurements, although the exposed film without any aging process was not thermally stable enough to measure the $\chi^{(3)}$ values. Formation of J aggregates after photochemical conversion from the spiropyran structure to the merocyanine structures cased considerable enhancement of the third-order optical nonlinearity.[9]

Various types of patterns may be formed by exposing the film to 366 nm light through black and transparent masks followed by aging at 30 °C for 12 h. Figure 4 shows one example of those patterns. The masked part remains transparent, while the exposed part changes into an intense blue color after the aging process at 30 °C. This pattern is quickly erased by heating the film to a temperature higher than 80 °C. It is supposed that J-aggregate structure is destroyed and forms molecularly dispersed merocyanine, and the thermally unstable merocyanine changes to transparent spiropyran under such high temperature. The reproduction of spiropyran after heating was preliminarily demonstrated by the recovery of the same absorption spectrum as the starting film. The cycle of J-aggregate formation and decoloration was repeated at least several times without any fatigue.

In conclusion, it was demonstrated that the third-order optical nonlinearity of polymer films can be reversibly con-

FIG. 4. Photograph of an image on the film reproduced by imagewise exposure to UV light followed by aging at 30 °C. Image part is transparent (low third-order nonlinearity); background (exposed area) is blue (high third-order nonlinearity).

trolled by the photochromic conversion and following *J*-aggregate formation of spiropyran embedded in an inert polymer matrix. Patterns consisting of areas with high and low third-order nonlinear optical activities were prepared by imagewise exposure of the photochromic films followed by a thermal treatment to form thermally stable *J* aggregates of photoinduced merocyanine in the exposed area. This system could be useful in developing new unconventional optical devices based on the optical nonlinearities, including new types of spatial light modulators.

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