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Toshio Sakai [a] , Hidetsugu Ikeda [a] , Yutaka Kawabe [a] & Kenji Kawasaki [a]

[a] Idemitsu Kosan Co. Ltd., Central Research Laboratories 1280, Kami-izumi, Sodegaura, Chiba, 299-02, Japan

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RESONANT THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF HEMICYANINE DOPED PMMA THIN FILM

TOSHIO SAKAI, HIDETSUGU IKEDA, YUTAKA KAWABE, and KENJI KAWASAKI
Idemitsu Kosan Co.Ltd., Central Research Laboratories
1280, Kami-izumi, Sodegaura, Chiba 299-02, Japan

Abstract The resonant third-order nonlinear optical properties of hemicyanine, 3-methyl-2-(6-morpholino-1,3,5-hexatrienyl)-benzoxazolium iodide (HC) doped polymethylmethacrylate (PMMA) thin films were measured by degenerate four-wave mixing (DFWM) at 580nm with 4ps pulses. It was found that the temporal profile of DFWM signal in 0.01M HC doped PMMA film was much different from that in dilute dimethylsulfoxide solution of HC. The decay of DFWM signal in the thin film consisted of the faster component (~10ps) in addition to the slower one (>100ps). The phase conjugate reflectivity was not proportional to the square of pump intensity and saturated even in the weak pump intensity. The effective $\chi^{(3)}_{xxxx}$ value of the thin film was relatively large (2.8×10^{-9}esu) at weak pump intensity (0.03μJ/pulse).

INTRODUCTION

The third-order nonlinear optical properties of conjugated organic materials have been studied extensively because of their large magnitude and fast response time.[1] It is well known that some organic dye molecules such as polyenes and cyanine dyes have very large third-order hyperpolarizabilities γ.[2–4]

Dye doped polymer, one of typical guest/host systems is very suitable for manufacturing nonlinear optical devices because of their good processabiblity and fabricability. Films with large third-order optical nonlinearirities $\chi^{(3)}$ and good optical quality could be obtained by doping of dye molecules with high concentration into amorphous polymers.[5-6] If molecules are enough separated from each other, it is predicted that nonlinear coefficients are proportional to the concentration of dyes. However, highly concentrated dye molecules usually show different spectroscopic properties from those of isolated molecules in dilute solution due to aggregation or crystallization in films. In these system, the nonlinear optical properties are also expected to be different from those of solutions. Therefore it is significant to study the

relationship between the dispersion state of molecules in polymers and $\chi^{(3)}$ value in order to design nonlinear optical devices, but such few studies have been made yet. There is also another interest to study the concentration dependence on the optical nonlinearity, because there are possibilities of the enhancement of $\chi^{(3)}$ which could be achieved by the delocalization of excited states or energy transferring due to dye aggregation.[7]

We have studied the resonant γ of conjugated organic molecules in solutions by degenerate four-wave mixing (DFWM) and have found that some cyanine dyes had large resonant γ ($\sim 10^{-28}$esu).[8-11]

In this paper, we report the resonant third-order nonlinear optical properties of hemicyanine, 3-methyl-2-(6-morpholino-1,3,5-hexatrienyl)-benzoxazolium iodide (HC) doped in polymethylmethacrylate (PMMA) thin films with high concentration. The temporal behavior and pump intensity dependence of DFWM signal were studied. The nonlinear optical properties of the films were discussed in comparison with those of dye solutions.

EXPERIMENTAL

(a) preparation of thin film

The molecular structure of HC is shown in Fig.1. HC doped PMMA thin films (HC/PMMA) were coated on glass substrates by casting, and were dried under vacuum circumstances to avoid solvent. Typical concentration of HC in PMMA was 0.01M. To characterize thin films, absorption and emission spectra were measured in visible

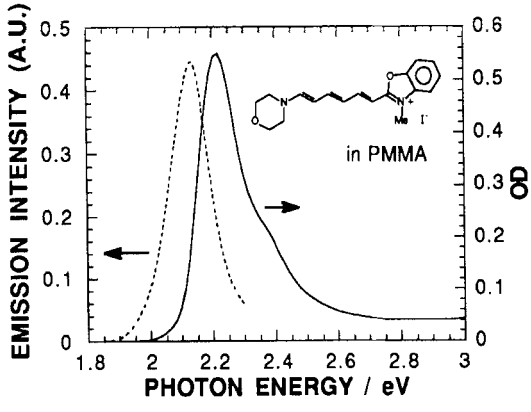

Fig.1 Absorption and emission spectra of HC/PMMA film (0.01M).

wavelength region. The thickness and surface roughness of films were measured by surface profiler (SLAN, DEKTAK 3030).

(b) measurement of third-order nonlinear optical properties

The third-order nonlinear optical properties of HC / PMMA were studied by using a phase conjugation configuration as shown in Fig.2. The strong laser pulses were obtained by the amplification of output pulses of a dye laser synchronously pumped by a frequency doubled mode-locked Nd:YAG laser (Spectra Physics model 3800S) in a three-stage pulse dye amplifier pumped by a frequency doubled 10Hz Q-switched Nd:YAG laser (Spectra Physics DCR-3G). The pulse duration was about 4ps, and energy per one pulse was 0.5 mJ. The pulse energy was attenuated to be less than 1μJ/pulse to avoid sample degradation by laser irradiation. For the present study, the wavelength of 580nm (2.138eV) was selected. Since the laser wavelength was in the absorption band, observed phase conjugate signal was originated mainly by resonant processes. The laser beam was split into three parts: two counterpropagating pump beams and probe beam were incident to the sample as shown in Fig.2. The forward pump beam and the probe beam were incident simultaneously and at a small angle (~6°) to the sample. The magnitude of the DFWM signal as a function of backward pump beam delay time (τ) was measured to investigate the dynamical process of the doped molecules. Moreover, phase conjugate reflectivity (Rpc) as a function of pump intensity was measured in order to estimate effective $\chi^{(3)}$ values of thin films at a fixed delay time. The experiments were conducted under the two kinds of polarization configuration. $\chi^{(3)}_{xxxx}$ value is obtained in the case that the polarization of all beams are parallel (parallel configuration), while $\chi^{(3)}_{xyyx}$ is obtained in the case that the polarization of the probe beam is perpendicular to those of the pump beams (perpendicular configuration).

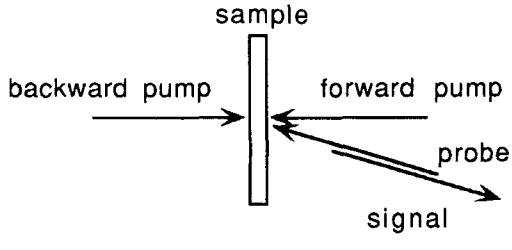

Fig.2 Beam arrangement in DFWM experiment.

The DFWM experiments were made for CS_2 and dimethylsulfoxide (DMSO) solution of HC (HC/DMSO) under the identical condition to compare with those of thin films. CS_2 and dye solution were set in a 0.5mm-thick fused silica cell.

RESULTS AND DISCUSSION

Absorption and emission spectra of HC/PMMA film are shown in Fig.1. The absorption band width is 0.18eV, and its peak energy is 2.21eV (560nm). In films with concentration of less than 0.01M, the profile and the peak positions of absorption and emission spectra were almost the same as those of a dilute DMSO solution ($\sim 10^{-4}$M). Therefore dye molecules seemed to be dispersed uniformly and isolated in PMMA films in this concentration region. However, some films had additive emission bands emerged in the infrared region and these feature strongly depends on the sample preparation. In this study, we used films without these additive emission bands. The surface roughness was farely good only in the central small area, where the typical thickness was about 17μm. Uniformity of thickness in that area was so good that the optical measurement was not influenced from the thickness variation.

The temporal profiles of DFWM signal of thin films were distinctly different from those of dilute solutions as mentioned below. Figure 3 shows the typical temporal profile of DFWM signal from HC/PMMA films in the parallel configuration with pump intensity=0.055μJ. The decay signal consisted of the slower component, the faster decay from τ=5ps to τ=50ps, and the coherence spike around τ=0ps. The time

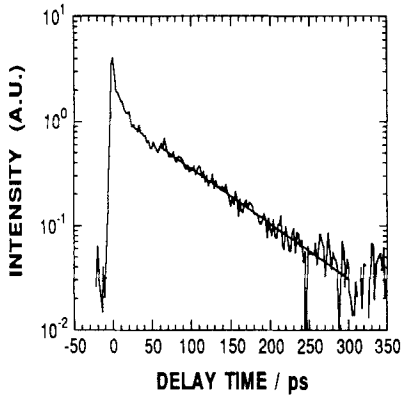

Fig.3 temporal profile of DFWM signal from HC/PMMA film. (parallel configuration)

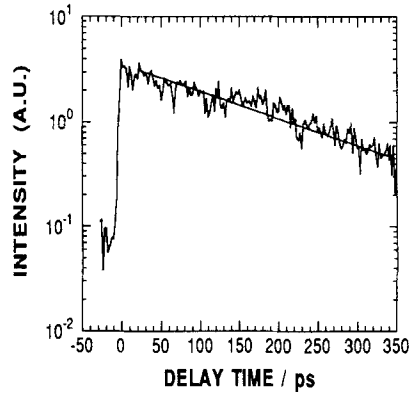

Fig.4 temporal profile of DFWM signal from HC/DMSO. (parallel configuration)

constant of the slower part was 82ps when it was assumed to be an exponential decay. However, the temporal profile strongly depended on the sample preparation. On the other hand, the temporal profile of DFWM signal from dilute HC/DMSO (1.91×10^{-4}M) in the parallel configuration is shown in Fig.4. In this case, the decay of signal was single exponential whose time constant was about 180ps, and the coherence spike was not clearly observed. By comparing these two profiles, there seems to be the excess relaxation channels with faster decay time in the thin films. It suggests the modification of the relaxation processes due to aggregation or crystallization in the HC/PMMA films which could not be recognized clearly from the absorption and emission spectra. It was confirmed that the difference of the temporal behavior between thin films and solutions was not due to the sample thickness, because we could not find any excess tail in the case of CS_2 whose decay time was well known to be 2 ps.

The temporal profiles of the HC/PMMA films and the HC/DMSO in the perpendicular configuration are depicted in Fig.5 and Fig.6, respectively. In both cases, signal shapes were basically similar to those in the parallel configuration. The decay of DFWM signal was nonexponential in thin films, while that was single exponential in solutions. In a two-level model, it can be shown by simple calculations that the decay of DFWM signal in the positive delay time is a half of the longitudinal relaxation time of the upper state.[12] However, as shown in DFWM signal decay in the films, no simple exponential decay was observed. The temporal profile of DFWM signal in this experiment was not able to be explained by a simple two-level model. Moreover, the decay time and the ratio of the faster component to the slower one strongly depend on the sample preparation. The

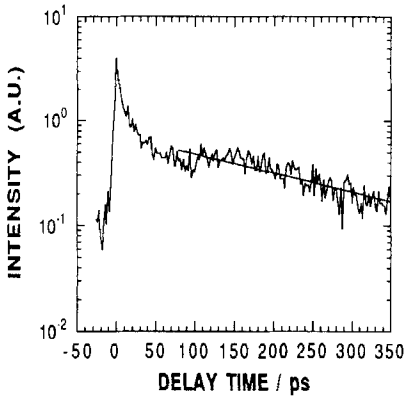

Fig.5 temporal profile of DFWM signal from HC/PMMA film. (perpendicular configuration)

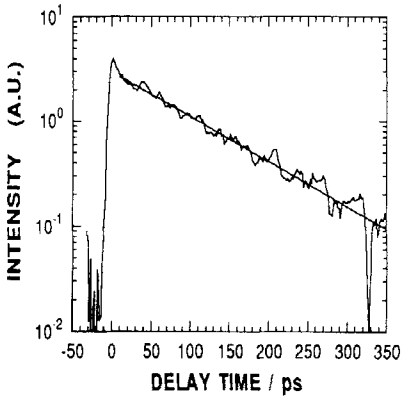

Fig.6 temporal profile of DFWM signal from HC/DMSO. (perpendicular configuration)

relaxation of dye molecules doped in films is very complex and sensitive to the dispersion state of molecules. Another transient measurement should be made to discuss DFWM signal decay in detail.

Figure 7 showed phase conjugate reflectivity *vs.* pump intensity in the parallel configuration for HC/PMMA, HC/DMSO, and CS_2. Closed and open squares were for HC/PMMA at τ=0 and 53ps, respectively. As known from Fig.3, the signals at τ=53ps were mainly attributed to the slower decay component. Open circles were for HC/DMSO, closed circles were for CS_2 as a reference. Except for CS_2, Rpc was not proportional to the square of pump intensity as expected in a $\chi^{(3)}$ process and was saturated at the pump intensity range used in this experiment. Comparing the behavior at τ=0 with that at τ=53ps, Rpc was saturated in the lower intensity in the latter case. It suggests that there are more than two relaxation processes with different time constants. These results are consistent with those in transient features. The magnitude of the effective $\chi^{(3)}$ at pump intensity 3×10^{-8}J/pulse (peak intensity 1MW/cm^2) were calculated by comparing with the results of CS_2 as a reference.

$$|\chi^{(3)}| = |\chi_{CS_2}^{(3)}| \left(\frac{n}{n_{CS_2}}\right)^2 \frac{L_{CS_2}\alpha}{e^{-\alpha L/2}(1-e^{-\alpha L})} \sqrt{\frac{R}{R_{CS_2}}} \quad , \qquad (1)$$

where parameters with subscripted CS_2 refers to the values of CS_2 and n is the

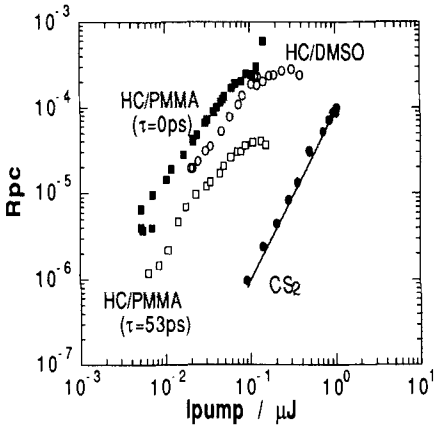

Fig.7 phase conjugate reflectivity *vs.* pump intensity. (parallel configuration)

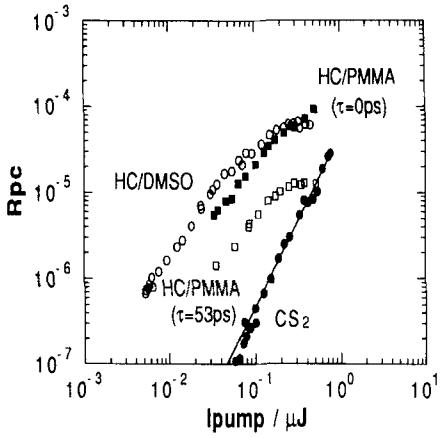

Fig.8 phase conjugate reflectivity *vs.* pump intensity. (perpendicular configuration)

refractive index, α is the absorption coefficient at 580nm, L is the sample length, Rpc is the phase conjugate reflectivity, n_{CS2}=1.64, L_{CS2}=0.05cm, $\chi_{CS2}^{(3)}{}_{xxxx}$=2.32x10^{-12}esu, $\chi_{CS2}^{(3)}{}_{xyyx}$=1.64x10^{-12}esu.[13]

$\chi^{(3)}{}_{xxxx}$ value of HC / PMMA film was 2.8x10^{-9}esu, and farely large because of the resonant enhancement effects. The magnitude of the effective γ_{xxxx} was estimated to be 1.2x10^{-28}esu by eq.(2).

$$\chi^{(3)}=Nf\gamma \qquad (2)$$

where f is the local field correction, in this paper we assume that the refractive index of PMMA was 1.5 to derive f(=$((n^2+2)/3)^4$)=4. N is the number density of molecules. On the other hand, from the same calculation the effective γ_{xxxx} was estimated to be 2.3x10^{-28}esu in dilute DMSO solution. From the fact that in both samples, the values of effective γ had the same order, it was found that the magnitude of nonlinearities γ were not seriously influenced from the difference of dispersion conditions of molecules with the concentration less than 0.01M.

Phase conjugate reflectivity as a function of pump intensty in the perpendicular configuration is shown in Fig.8. The similar intensity dependence to those in the parallel configuration was observed. From the same analysis, in the perpendicular configuration, the effective $\chi^{(3)}$ values of films were estimated in films and $\chi^{(3)}{}_{xyyx}$=7.0x10^{-10}esu, γ_{xyyx}=2.9x10^{-29}esu. In DMSO solutions, γ_{xyyx}=1.3x10^{-28} esu. The ratio of tensor component $\chi^{(3)}{}_{xxxx}/\chi^{(3)}{}_{xyyx}$ in the thin film was about 4 which was close to the expected value 3 in the case of a pure electronic process. Therefore, $\chi^{(3)}$ mainly due to the electronic process, the saturation of absorption was measured.

CONCLUSION

The resonant third-order nonlinear optical properties of hemicyanine doped PMMA thin films were investigated by picosecond DFWM. It was found that the temporal profile of DFWM signal in 0.01M HC doped PMMA film was much different from that in dilute dimethylsulfoxide solution of HC. The decay of DFWM signal in the thin film consisted of the faster component (~10ps) in addition to the slower one (>100ps). On the other hand, phase conjugate reflectivity was not proportional to the square of the pump intensity and saturated even in the weak pump intensity. In HC/PMMA film (0.01M), the effective $\chi^{(3)}{}_{xxxx}$ was estimated to be 2.8x10^{-9}esu at weak pump intensity.

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