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Phase Conjugation in Saturable Absorbing Dye Films by Degenerate Four-Wave Mixing and Holographic Processes Using Nanosecond Pulse and CW Lasers

Hiromasa TANAKA, Akira HORIKOSHI, Hirofumi FUJIWARA* and Kazuo NAKAGAWA

Department of Materials Science and Engineering, Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan

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We report on the simultaneous generation of phase-conjugate signals by degenerate four-wave mixing (DFWM) and holographic processes using a nanosecond pulse and a CW lasers in polyvinyl alcohol (PVA) films doped with four kinds of saturable absorbing dyes. For the pulse laser, of the four kinds of dye-doped PVA films, the erythrosine B-doped PVA and uranine doped-PVA films generate PC signals only by the DFWM process, while the other dye-doped PVA films generate PC signals simultaneously by not only the DFWM process but also the holographic process. Especially, the safranin T-doped PVA film generates strong PC signals by the holographic process. In contrast, all of the dye-doped PVA films generate the two types of PC signals for the CW laser. The fading of dye molecules is found to result in the generation of the holographic component of PC signals which governs the temporal behavior of the total PC signals.

Key words: degenerate four-wave mixing, dye-doped polymer films, saturable absorbing dye, nanosecond phase conjugation, fading of dye molecules

1. Introduction

Phase conjugation by degenerate four-wave mixing (DFWM) is attractive for applications to real-time optical image processings[1–3] and phase-conjugate (PC) interferometries[4,5] because a phase matching condition can be satisfied for a wide field of view. Organic dye-doped polymer films are candidate materials as a phase conjugator. Compared with other nonlinear materials such as oxide crystals, semiconductors, liquid crystals, etc., the dye-doped films have the advantage of easy fabrication of large size elements and provide a wide variety of dye/polymer combinations which enable us to develop functional phase conjugators suitable for many practical applications. In the experiments of PC signal generation using a CW argon-ion laser, we revealed that xanthene dyes (fluorescein, eosin Y and erythrosine B)-doped polymer films can generate PC signals simultaneously by not only the DFWM process but also the holographic process under the condition that the polarization states of a probe and two pump beams are mutually parallel.[4–6] The PC signals by DFWM process with response time of ~ms result from saturable absorption in dye molecules,[7,8] while the PC signals by the holographic process with response time of ~s are generated from a hologram recorded in dye-doped polymer films. The holographic process arises from irreversible photochemical changes in the absorption and/or refractive index in dye molecules. We call these two types of PC signals the DFWM component and the holographic component. Using a combination of the two types of PC signals, we demonstrated the application of PC signals to PC interferometries[4,5] using a CW argon-ion laser. However, if only the DFWM component of PC signals is preferable in dye-doped polymer films, the generation of the holographic component must be suppressed. In saturable absorbing dye-doped polymer films, this can be achieved by setting the polarization state of a probe beam orthogonal to two pump beams.[3]

From a practical viewpoint, pulse lasers are required for rapid information processing. We expect that, like the PC signal generation using a CW laser, dye-doped polymer films could also generate the two types of PC signals if a nanosecond pulse laser were used. Our main purpose is to examine this using a nanosecond pulse laser in a conventional DFWM configuration. The two types of PC signal generations using a CW laser are also examined for comparison with the results using the pulse laser. In addition, experiments are performed on the fading of dye molecules under the irradiation of a nanosecond and a CW lasers in order to study the effect of the fading of dyes on the temporal behavior of PC signals.

2. Experimental

Figure 1 shows the experimental setup for measuring the generation of two types of PC signals. An optical parametric oscillator (OPO) pumped with a Q-switched Nd:YAG-laser was used as a pulse source at 515 nm with a linewidth of 0.2 cm^{-1}; this wavelength is the same as that of an argon-ion laser. The pulsewidth is ~5 ns (FWHM) and the repetition rate is 10 pulses/s. The polarization states of a probe and two pump beams were mutually parallel and s-polarized (linearly polarized normal to the plane of the optical table). Two optical delay lines (TDL1, TDL2) are inserted in the optical paths of a probe beam (Epr) and a backward pump beam (Eb) so that the optical path lengths of the three beams coincide at a dye-doped polymer film. A shutter (S) is used to turn off the probe beam, an interference filter (IF) being used to eliminate fluorescence and phosphorescence emitted from the dye-doped film. The fluences of the two pump beams and the probe beam are set at 1.3 mJ/cm^2. The PC signal is detected as time-averaged power by a combination of a photodetector (PD) and a low-pass filter (LPF) with a time constant of ~0.3 s.

Polyvinyl alcohol (PVA) films doped with four kinds of saturable absorbing dyes: rhodamin 6G (R6G), uranine

*E-mail: h-fuji@mmm.muroran-it.ac.jp

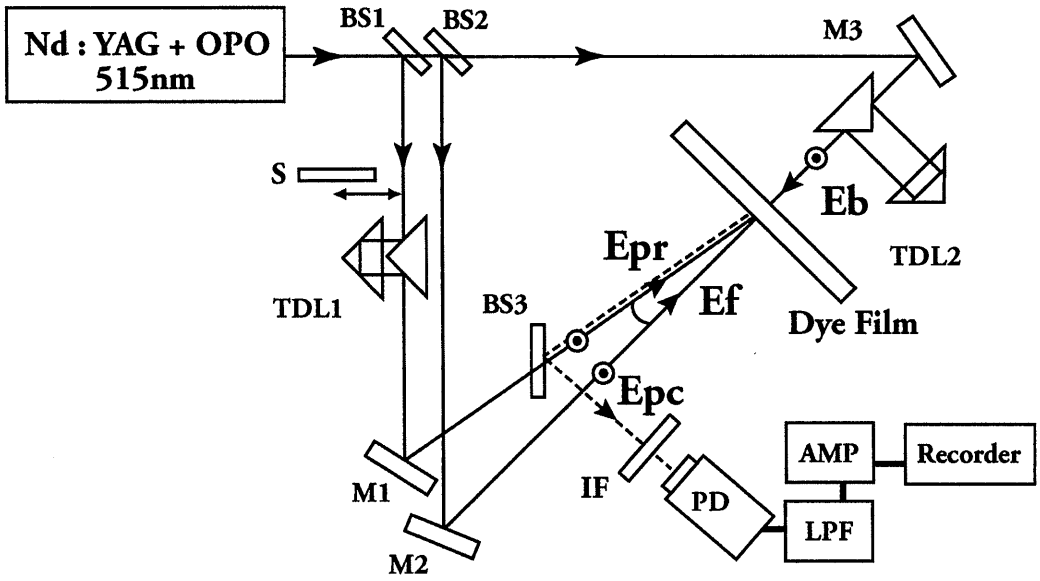

Fig. 1. Experimental setup for DFWM process. M1, M2, M3, mirrors; BS1, BS2, BS3, beam splitters; TDL1, TDL2, optical delay lines; S, shutter; IF, interference filter; PD, photodetector; LPF, low pass filter; AMP, amplifier; Ef, forward pump beam; Eb, backward pump beam; Epr, probe beam; Epc, phase-conjugate beam.

(UR), erythrosine B (EB) and safranin T (ST) are used as dye-doped polymer films. The reasons for choosing these dyes are that R6G is most frequently used in PC signal generation using a pulse laser, while the other dyes are generally used as saturable absorbing dyes using a CW laser. The four kinds of dye-doped PVA films were prepared as follows. PVA powder was dissolved in dimethyl sulfoxide (40°C) to which an appropriate amount of dye was added so that optical density $\alpha_0 L$ (product of the small-signal absorption coefficient and the film thickness) at 515 nm of each dye-doped film takes ~2.0; this value is empirically adequate for PC signal generation in saturable absorbing dye-doped polymer films using a CW laser source. The dye-doped PVA film was made by pouring the solution onto a glass plate and drying it in an oven, keeping it at a temperature of 34°C and a humidity of 50% for four days. Then, the dye-doped PVA film was baked in the oven at 80°C for 1 h to remove the anisotropy induced when the PVA solution was spread over the glass plate. The resultant films were about 60 μm in thickness. The absorbance spectrums of the four kinds of dye-doped PVA films are shown in Fig. 2. The optical densities $\alpha_0 L$ at 515 nm are 1.9, 2.2, 2.0 and 2.3 for the EB/PVA, R6G/PVA, ST/PVA and UR/PVA films, respectively.

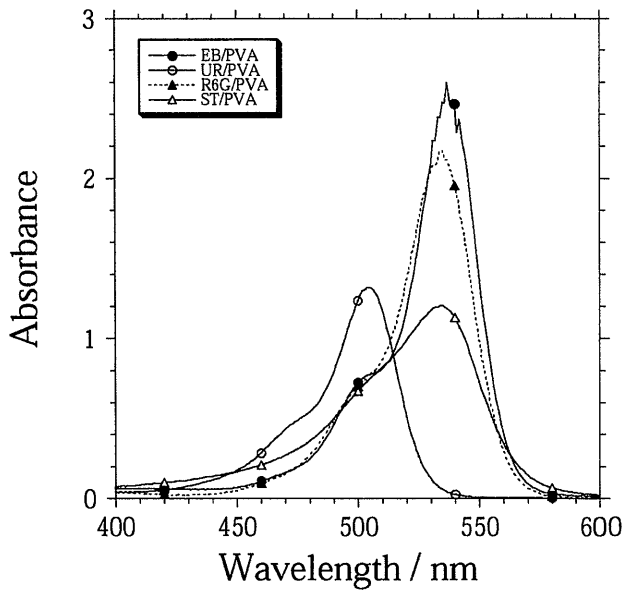

Fig. 2. Absorbance spectrums of the four kinds of dye-doped PVA films.

3. Results and Discussion

3.1 Two types of PC signal generation using a nanosecond pulse laser

We first exhibit experimentally the method for examining whether dye-doped PVA films could generate two types of PC signals, that is, the DFWM and holographic components. Figure 3 shows a typical example of the decay of time-averaged PC signal when the probe beam was turned off. At time A the probe beam was turned off. The PC signal is found to initially decay fast, followed by a slower decay. Here, E_D and E_H stand for the complex amplitude of the DFWM and holographic components, respectively. The PC signal with a fast decay corresponds to $|E_D + E_H|^2 - |E_H|^2$: the total PC signal results from the interference between the DFWM and holographic components. The PC signal with a slow decay is the holographic component $|E_H|^2$ because it appears even in the absence of the probe beam. The two pump beams were turned off at time B and were again turned on at time C 4 minutes after B. At time C the PC signal (holographic component) recovered up to almost the magnitude obtained at time B, and then decreased gradually. This result indicates that the information formed by the two

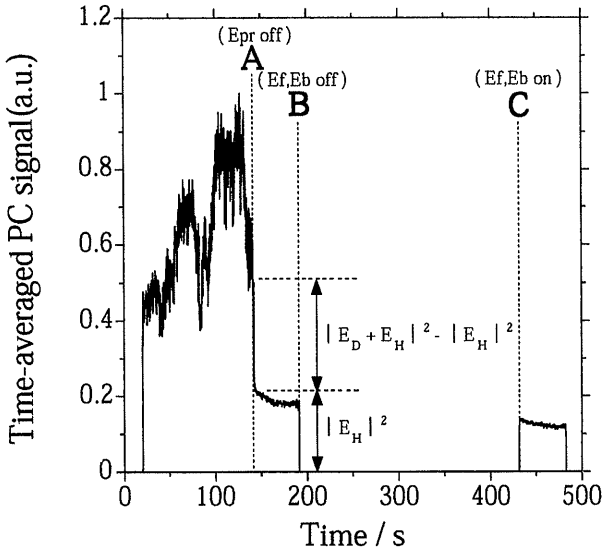

Fig. 3. Decay of time-averaged PC signal when the probe beam is turned off. The fast and slow decays correspond to the DFWM and holographic processes, respectively.

pump and probe beams is recorded as a hologram in the dye-doped PVA film and the stored information is gradually erased by reading with each pump beam. If only the DFWM component of PC signals is generated, the vertical line exhibiting the fast decay of the DFWM component falls to zero level. Thus we can examine the generation and growth of the holographic component by intermittently chopping the probe beam during a period sufficiently shorter than the decay time of the holographic component while PC signals are generated.

We performed experiments on the temporal behavior of PC signals which may consist of the two signal components. The temporal behavior of PC signals was observed by intermittently chopping the probe beam for 1 s at every 10 s period for the four kinds of dye-doped PVA films. The experimental results are shown in Fig. 4, where the time-averaged PC signal power is expressed as an arbitrary unit. As the scale of the vertical axis is the same for each figure, the growth of the holographic component of PC signals can be compared. For the total PC signal power involving the DFWM and holographic components, however, it makes no sense to compare them with each other. This is because the reflectivity of the DFWM component of PC signals in saturable absorbing dye-doped polymer films depends significantly on the intensity of the pump beam, the optical density of the dye-doped film and the relation between the wavelength used as a light source and the absorption peak of a given dye-doped film.[9]

The EB/PVA and UR/PVA films generate only the

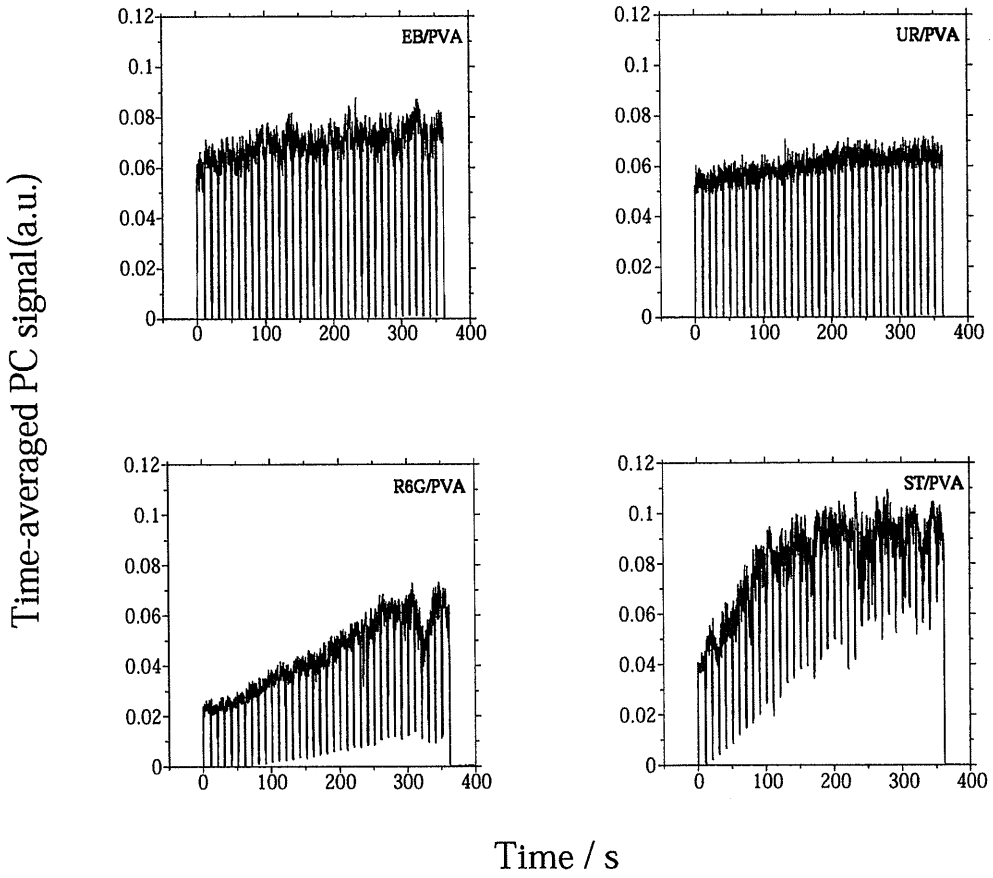

Fig. 4. Temporal behavior of time-averaged PC signals generated from the four kinds of dye-doped PVA films using the nanosecond pulse laser at a wavelength of 515 nm. The probe beam is intermittently chopped during 1 s every 10 s period. The scale of the vertical axis is the same for each figure.

DFWM component of PC signals, while the other dye-doped PVA films generate PC signals simultaneously by both the DFWM process and the holographic process. Especially, the ST/PVA film strongly generates the holographic component. Of course, all of the dye-doped PVA films could generate the two types of PC signals for more intense fluence of pump beams. These results show that, of the four kinds of dye-doped PVA films, the ST/PVA film is most suitable for PC interferometries, while the EB/PVA and UR/PVA films are good for applications requiring only the DFWM component of PC signals. In many practical applications, the temporal response of a PC signal is a factor as important as its reflectivity. In this experiment, however, detailed information on the rise and decay time of the DFWM component of PC signals can not be obtained.

It is very interesting to note that the EB/PVA film generates only the DFWM component using the pulse laser, although it was able to generate simultaneously the two types of PC signals using a CW argon-ion laser in our past experiments.[4] We infer that the holographic component of PC signals results from the fading of dye molecules which is strongly dependent on whether the light source is a pulse laser or a CW laser.

To examine the relation between the growth of the holographic component and the fading of dye molecules, the relative changes in the optical density $\Delta\alpha_0 L/\alpha_0 L$ were measured using a pump-probe method for the four kinds of dye-doped PVA films. The same nanosecond pulse laser as used in the previous experiment was used as an irradiating beam at a fluence of 1.3 mJ/cm^2. The transmittance was measured using sufficiently weak CW laser beams as a probe beam at wavelengths of 532 nm and 488 nm for EB/PVA, R6G/PVA and ST/PVA films and UR/PVA film, respectively. The reason for using the two laser beams is that the absorption peaks of the dye-doped PVA films belong roughly to two groups as seen from Fig. 2. We confirmed experimentally that the absorbance spectrum of dye molecules in PVA films indicated homogeneous broadening, so that the use of a different wavelength has no effect on the relative change $\Delta\alpha_0 L/\alpha_0 L$. In the experiments, the pump beam was intermittently turned off during the measurement of the transmittance to avoid the influence of saturable absorption of dye molecules.

Figure 5 shows the relative change in the optical density $\Delta\alpha_0 L/\alpha_0 L$ as a function of irradiation time for each dye-doped PVA film. The relative change $\Delta\alpha_0 L/\alpha_0 L$ is small for the EB/PVA and UR/PVA films which generate only the DFWM component of PC signals, while that for the ST/PVA film is the largest, which most strongly generates the holographic component. The fading of dye molecules is thought to be responsible for the generation of the holographic component of PC signals.

3.2 *Two types of PC signal generation using a CW laser*

In past experiments,[4,5] we showed that EB/PVA and eosin Y-doped gelatin films simultaneously generated the two types of PC signals using a CW argon-ion laser. Comparing these results with those for the nanosecond pulse laser, it is interesting to examine whether the other three

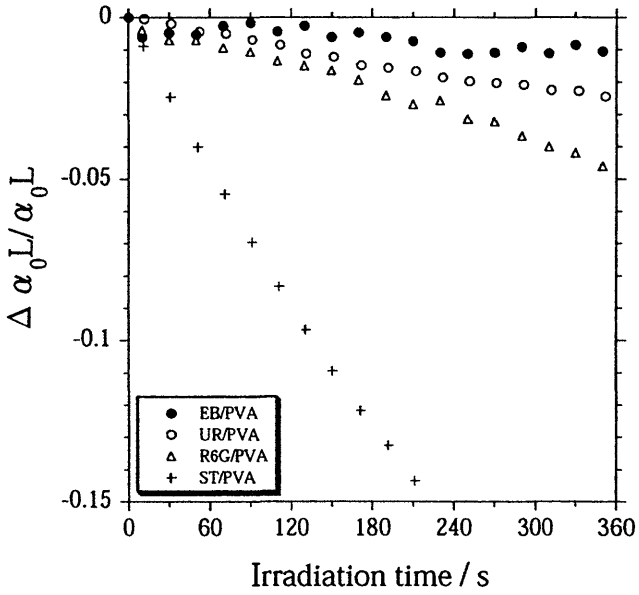

Fig. 5. Relative change in the optical density $\Delta\alpha_0 L/\alpha_0 L$ of the four kinds of dye-doped PVA films under the irradiation of the nanosecond pulse laser at a fluence of 1.3 mJ/cm^2.

kinds of dye-doped PVA films except for the EB/PVA film can simultaneously generate the two types of PC signals for a CW laser. Therefore, the experiments were performed on the two types of PC signal generation using a CW argon-ion laser at a wavelength of 515 nm in a conventional DFWM configuration.[4] The intensities of the two pump beams and the probe beam are set at 1.0 W/cm^2 and 0.3 W/cm^2, respectively. The experimental results for the four kinds of dye-doped PVA films are shown in Fig. 6, where the PC signal power is normalized with the maximum PC signal power. The reasons for this are that our main interest is in the simultaneous generation of the two types of PC signals rather than the reflectivity of each dye-doped PVA film, and that the relation between the temporal behavior of the PC signals and the relative change $\Delta\alpha_0 L/\alpha_0 L$ can be clearly represented.

All of the dye-doped PVA films can generate simultaneously the two types of PC signals; furthermore, the total PC signals decrease gradually after reaching a maximum. We attribute the decrease in total PC signals to the fading of dye molecules. The temporal behavior of the total PC signals represents a similar tendency to that of the holographic component. This is because constructive interference occurs between the DFWM and holographic components; in the absence of the holographic component (the polarization state of a probe beam is orthogonal to two pump beams), PC signals decrease gradually owing to the fading of dye molecules.[3] The decrease in the holographic component may be due to the contrast saturation of holographic gratings by the proceeding of the fading of dye molecules. If the destructive interference occurs between the DFWM and holographic components, PC signals will increase when the probe beam is turned off. In fact, we observed such a phenomenon in the experiments of PC signal generation. It should be noted that the decrease in the total PC signals of

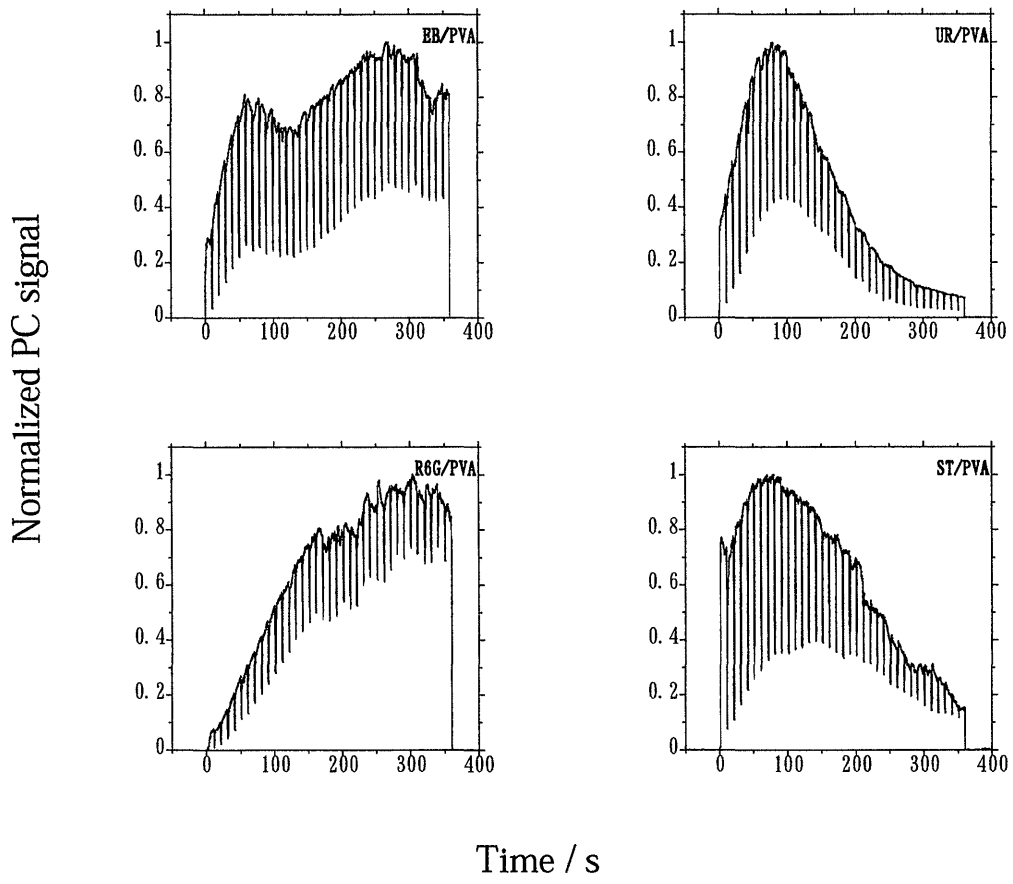

Fig. 6. Temporal behavior of PC signals generated from the four kinds of dye-doped PVA films using the CW argon-ion laser at a wavelength of 515 nm. The probe beam is intermittently chopped during 1 s every 10 s period. The PC signal power is normalized with the maximum PC signal power.

the UR/PVA film is significant for the CW laser, although the UR/PVA film generates only the DFWM component of PC signals for the nanosecond pulse laser (see Fig. 4).

The fading of dye molecules under the irradiation of a CW laser beam at an intensity of 1 W/cm^2 was also examined. The experimental setup and procedure are the same as that for the pulse laser except that a CW argon-ion laser is used as a irradiation beam. Figure 7 shows the relative change in the optical density $\Delta\alpha_0 L/\alpha_0 L$ as a function of irradiation time for each dye-doped PVA film. In this figure, the data are plotted from 30 s after the initiation of pump beam irradiation because the unstable phenomena are observed right after the irradiation for the UR/PVA and R6G/PVA films. The experimental results differ greatly from those for the pulse laser. For example, the fading of dye molecules of the UR/PVA film is the largest for the CW laser beam, although it is small for the pulse laser. The fading of dye molecules results from an irreversible photo-oxidation via the excited state energy levels of dye molecules. Therefore, we infer that the singlet and triplet states of dye molecules associate mainly with the photo-oxidation for the pulse and CW laser irradiations, respectively.[10] Of course, the relative change $\Delta\alpha_0 L/\alpha_0 L$ for each dye-doped film by the CW laser is greater than that by the pulse laser because the irradiation energy per second of the CW laser is as much as ~70 times greater than that of the pulse laser. The experimental results

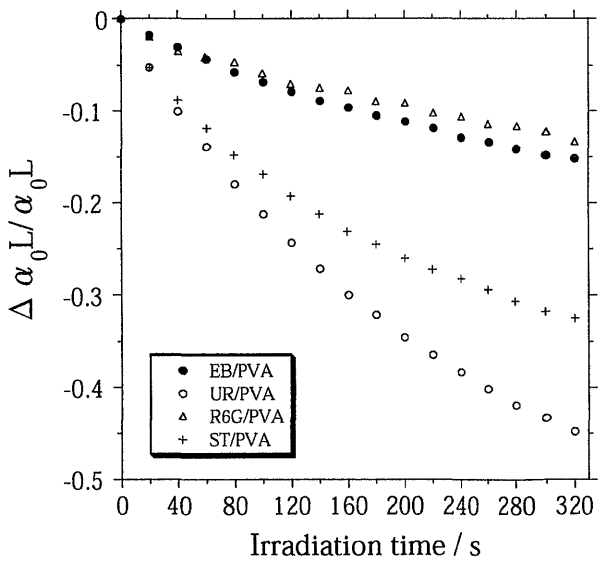

Fig. 7. Relative change in the optical density $\Delta\alpha_0 L/\alpha_0 L$ of the four kinds of dye-doped PVA films under the irradiation of the CW argon-ion laser at an intensity of 1 W/cm^2.

of PC signal generation and the fading of dye molecules using the pulse and CW lasers for the UR/PVA film suggest that the growth of the holographic component depends

strongly on the fading of dye molecules. Furthermore, a good correspondence can be recognized between the normalized PC signal power 6 minutes after the initiation of PC signal generation (the end of the experimental data) and the relative change $\Delta\alpha_0 L/\alpha_0 L$ for each dye-doped PVA film. We believe from these facts that the fading of dye molecules leads to the generation of the holographic component which governs the temporal behavior of the total PC signals. In our experiments on the PC signal generation using the pulse and CW lasers, the significant growth of the holographic component of PC signals for the CW laser may arise from more intense irradiation energy of the CW laser than that of the pulse laser.

4. Conclusions

We have examined the two types of PC signal generation (the DFWM and holographic components) by a nanosecond pulse and a CW lasers in the PVA films doped with four kinds of saturable absorbing dyes using a conventional DFWM configuration. In addition, experiments on the fading of dye molecules were performed to study the relation between this fading and growth of the holographic component of PC signals.

In the experiments on PC signal generation using the nanosecond pulse laser, of the four kinds of dye-doped PVA films, the EB/PVA and UR/PVA films generate only the DFWM component of PC signals, while the other dye-doped PVA films generate PC signals simultaneously by both the DFWM process and the holographic process. Especially, the ST/PVA film strongly generates the holographic component. In experiments using the CW argon-ion laser, all of the dye-doped PVA films simultaneously generate the two types of PC signals. The relation between the fading of dye molecules and the growth of the holographic component of PC signals indicates that the fading of dye molecules leads to generation of the holographic component which governs the temporal behavior of the total PC signals.

Organic dye-doped polymer films are expected to be used as functional phase conjugators for not only CW laser sources but also nanosecond pulse laser sources.

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