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Preparation of the Intracavity-grade Thin Film Using an Optically Nonlinear Organic Compound for the Pulsed Laser Light Compression

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The 2-methyl-4-nitroaniline(MNA)-doped polymethyl methacrylate (PMMA) film was prepared for intracavity pulse compression of a short pulse laser. This organic film held between two cover glasses was formed by means of an evacuated hot-press apparatus. The ultrafast response to a femtosecond light pulse was observed, which shows 3rd order nonlinear optical effects.

Optically nonlinear effects are being widely utilized, e.g., for an up-conversion of laser light frequency by using inorganic crystals like KDP(potassium dihydrogenphosphate). Some organic compounds such as urea have also been investigated for a long time, because of their large optical nonlinear susceptibility and their flexibility in designing of new materials with larger susceptibilities.[1] Furthermore, it is believed that the organic compounds would possess a larger light power threshold against dielectric breakdowns and, also, a faster response to ultrashort light pulses, since the nonlinearity of most organic compounds is caused only by an electronic polarization in the molecules irrelevant to a lattice polarization. The organic compounds with 2nd order nonlinearity, usually, possess long or large conjugated π-electron systems which can induce a large electronic polarizability due to electron donating and accepting substituents in the molecule. As for 3rd order nonlinear effects, however, with which we will be concerned hereafter, no specific guiding principle to analyze and develop new materials has been established, although many interesting 3rd order effects have already been discovered and studied.

To investigate the 3rd order nonlinear interaction of optically functional molecules with incident light, (mono-)molecularly dispersed systems in polymer matrices are very useful. The well-known method of thin film formation is the so-called film cast method using slow evaporation conditions of solvents from a solution. In this method, it is easy to make relatively thick($\approx$1 μm), apparently clear, flat, and smooth monomolecularly dispersed films. Even though the clear and smooth film in appearance could be obtained by this method, it did not have sufficient optical quality to maintain the phase of the transmitting light wave; even in the cast film with making most careful evaporation of the solvents, the solvent vapor in the cast film often caused micropores and/or bubbles

inside the film, and these acted really as scattering centers to the incident light wave. Therefore, we had to develop a new method for obtaining good-quality organic film tolerable enough to be used for the nonlinear optical applications.

MNA has, until now, been investigated mainly as 2nd order optically nonlinear material and has been known to have a 22-time larger SHG efficiency than urea.[2] We adapted MNA as a starting compound to demonstrate our new method because of its well-known properties. The other properties of MNA are summarized as follows: the space group of the crystal, monoclinic ($P2_1$); MW, 152.15; mp, 131-133 ℃; transparent between 470 nm and 1.8 μm; the threshold power for dielectric breakdown, 200 MW/cm^2 at 1.06 μm. The bright yellow powder crystals of MNA with two purification steps were employed: 3 times recrystallization from commercial MNA[3] with purified ethanol, as the 1st step; 5 times sublimation under 10^{-3} Torr vacuum, as the 2nd step. We chose PMMA with a mean degree of polymerization of about 10^4 as a matrix polymer, and it has a glass transition temperature (Tg) of 105 ℃. Since the temperatures for softening, casting and degrading to monomer are 80-125 ℃, 120-160 ℃ and 160-300 ℃, respectively, the solute nonlinear material with melting points of 100-150 ℃ is applicable to the "hot-press" thin film formation in PMMA. We have chosen this hot-press treatment under vacuum as the best method for obtaining a quartz-like optical quality thin film without any pores, because this is a completely solvent-free film formation process. The other advantage of this treatment under vacuum, which is readily recognized, is its ability to reduce the oxidation of a sample under the heating process. The hot-press apparatus employed here has two additional heating rams which directly press the sample and the vacuum chamber inserted between these two rams. Except for the above modification, the press system is basically the same as commercial one. The specifications of our apparatus are an ultimate pressure of 100 kg/cm^2, maximum temperature of 300 ℃ and ultimate pressure of 10^{-3} Torr. First, both MNA and PMMA were weighed to appropriate molar ratios, and then, were mixed and ground in a mortar for a sufficient amount of time(several tens of minutes). This powder mixture was inserted between two cover glasses and was set in the vacuum hot-press apparatus. After pumping down for 10 min, we started heating at the rate of 10 deg/min up to 150 ℃ [about 20 deg higher than melting point of MNA(131 ℃)]. The sample was pressed up to 50 kg/cm^2 and was kept at the temperature and pressure for 10 min; then we released the pressure and allowed the sample to cool down slowly(3 deg/min). MNA was soluble in PMMA up to 70 mol%. The film with the concentration of less than 60 mol% was very stable. The produced sample, looking like very clear film, had a little fluctuation in its transmittance revealed by microscope inspection, which may result from included opaque particles. The dimensions and properties of the sample are shown in Fig.1. We believe that the excellent organic thin film for nonlinear applications has been obtained.

We suppose that the intracavity femtosecond pulse compression would become a convenient and sensitive detection method of optically nonlinear responses due to inserted organic or inorganic materials.[4-6] Although the detection of nonlinear effects by CPM(Colliding Pulse Modulation) laser proposed here is very sensitive, it must be remem-

bered that it is short of the direct estimation of the nonlinear refractive index and of the correlation with other optical properties. The CPM laser having 0.353 m cavity length constructed with 8 mirrors and 4 prisms was employed for the present experiment; the 3rd mirror pair was added to a normal cavity arrangement.[6,7] As the waist size of laser beam at the confocal point of the mirror pair used for sample setting was about 10 $\mu m\phi$ and 30 μm in length, the homogeneity of the sample, such as in smoothness, clearness and the concentration of dispersed molecules, is essential for efficient interaction with an incident laser beam in this volume. The optical density of the sample at an oscillation wavelength of 625 nm must practically be lower than 0.025. The nonlinearity estimation of the sample measured in the cavity of the CPM laser was performed according to the equation in Ref. 4,7; the decrease in the pulse width compressed by the organic sample is determined mainly by the magnitude of the nonlinear refractive index n_2. The n_2 value would become large enough for the pulse compression experiment, only if it is more than 100 times as large as the value of ethylene glycol.[4,7] The MNA concentration dissolved in PMMA matrices was another important parameter, and was set to be about 50-60 mol% in the present experiment. The optical quality of the sample is the most important constraint for laser oscillation, requiring high grade transmittance, flatness, smoothness and homogeneity like glass plate. As for the transmittance, the particle and/or bubble density unexpectedly introduced in the sample should be as low as possible not to reflect or scatter the incident laser beam. While the shortest pulse width with no sample in the laser cavity was 49 fs, the pulse width shortened after inserting the MNA doped PMMA thin film to 32 fs as is shown in Fig.2. These results indicate that 3rd order optical nonlinear effects are observed without any experimental ambiguity. It is essential that this organic film was able to respond to light intensity changes in the order of tens of femtoseconds, since the repetitive light pulse being built up in the CPM laser cavity was such a short one as well as was compressed. In the usual cast film, micropores of almost the same size as the incident laser beam diameter(10 $\mu m\phi$) are observed contrary to the hot-pressed film. These defects exhibited a large scattering effect and prevented to start the oscillation of the CPM laser. Sample damages due to laser irradiation were found and microscopically analyzed. After operating the CPM laser with the sample inserted, the laser oscillation became gradually unstable, and then stopped in several minutes. Such damage was detectable by means of microscopic absorption spectrum analysis. The spot of the sample irradiated by a focused laser beam in the cavity for several minutes exhibited an additional lower energy tail to an intrinsic absorption spectrum(Fig.3). This damage was drastically decreased by further purification, and the improvement regarding the purification procedures is now being carried out in our laboratory. Considering such optical damage, suitable organic compounds tolerant to intense laser irradiation must be produced. We think, therefore, that a stable and defectless single crystal of organic thin film would be the ideal material to prevent damage due to laser irradiation, though our method might be the best at present.

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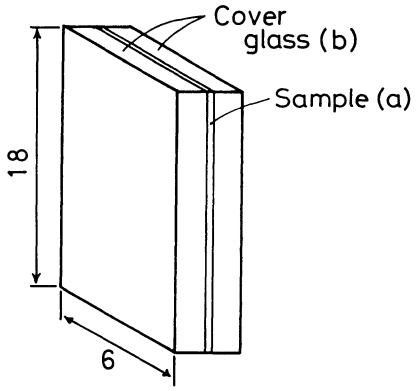

Fig. 1. The sample formed by the hot-press method: a. 30 μm-thick MNA/PMMA film, whose MNA concentration is 50-60 mol%; b. 150 μm-thick cover glass, whose dimensions are 18 x 6 mm. The nonlinear refractive index n_2 is 2.6×10^3 times as large as that of ethylene glycol.

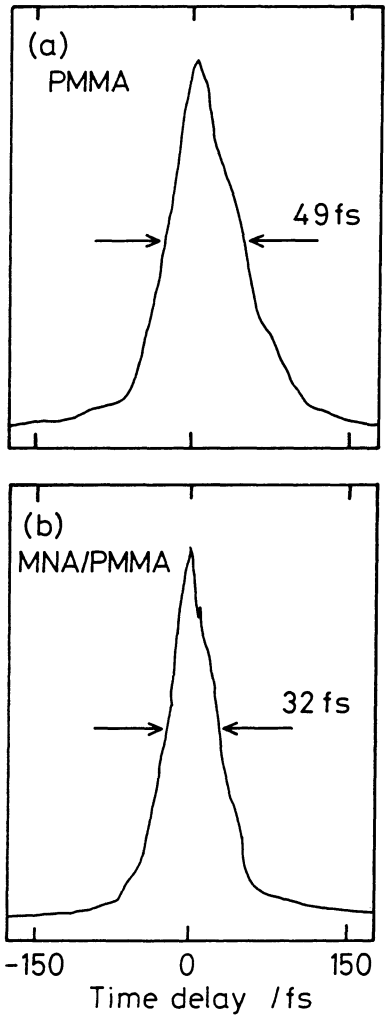

Fig. 2. The pulse width of 49 fs (a) with no sample inserted was reduced to 32 fs (b) after insertion of the MNA/PMMA film.

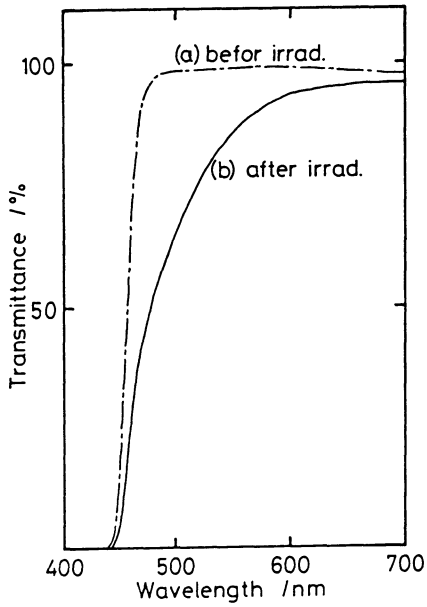

Fig. 3. Absorption spectra of the MNA/PMMA sample before irradiation (a) and after irradiation (b). Additional lower energy tail to the intrinsic absorption spectrum was observed.

References

1) D.J.Williams, Angew.Chem.,Int.Ed.Engl., 23, 690 (1984).
2) B.F.Levine, C.G.Bethea, C.D.Thurmond, R.T.Lynch, and J.L.Bernstein, J.Appl.Phys., 50, 2523 (1979).
3) Wako Pure Chemical Industries, Ltd.
4) R.S.Miranda, G.R.Jacobovitz, C. H.Brito Cruz, and M.A.F.Scarparo, Opt.Lett., 11, 224 (1986). The nonlinear refractive index n_2 of ethylene glycol is $n_{2.EG} = 3 \times 10^{-16}$ $cm^2/W = 7 \times 10^{-14}$ esu.
5) S.Ducharme, W.P.Risk, W.E.Moerner, V.Y.Lee, R.J.Tweig, and G.C.Bjorklund, to be published in Applied Physics Letters.
6) M.Yamashita, K.Torizuka, and T.Sato, Opt.Lett., 13, 24 (1988).
7) M.Yamashita, T.Hiraga, H.Matsuda, K.Torizuka, S.Okada, T.Moriya and H.Nakanishi, to be published in Opt.Commun. (1990).

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