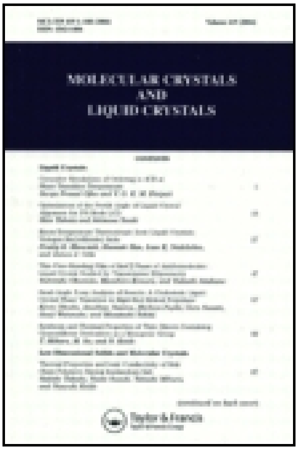

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# Properties of the Optically Nonlinear Organic Material Densely Doped in Matrices

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# Properties of the Optically Nonlinear Organic Material Densely Doped in Matrices [1]

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Abstract Optical properties of densely doped organic optically nonlinear materials were investigated by means of optical absorption spectroscopy, optical harmonics generation, X-ray diffraction spectroscopy and pressure tuning spectroscopy. From the investigation of the absorption $\lambda_{max}$, 2-methyl-4-nitroaniline(MNA) in poly methyl methacrylate(PMMA) exhibited an intermediate character between the crystal and the MNA dissolved in the solvents, i.e., some type of "amorphous", and in the regenerated cellulose(cellophane) almost the same character as the MNA crystal. These results were consistent with the X-ray diffraction analysis, the second and third harmonics generation and the pressure effect on the absorption $\lambda_{max}$ and fwhm.

## Introduction

For more than two decades, optically nonlinear phenomena in organic compounds such as urea, MNA[2] and so on[3] have been widely investigated because of the large optical nonlinear susceptibility, the fast response to ultrashort light pulses and the high light-power durability against dielectric breakdowns.

In recent studies on the organic compounds, design and synthesis of new materials possessing larger nonlinear susceptibilities are efficiently performed through comprehension of the origin and mechanism of optical nonlinearity. This development has been also stimulated by a measurement that analyzes the time response to ultrafast light pulses such as pulse compression in the intracavity of a femtosecond pulsed laser with insertion of third-order nonlinear organic compounds.[4,5]

The well-known methods for estimating harmonics generation are the "Maker fringe method" for single crystal samples,[6] and the "powder harmonics generation method" for as-synthesized compounds or ground crystals.[7] For the purpose of elucidating the mechanism of nonlinear phenomena, the powder method is quite insufficient because the optical and chemical qualities of the sample are not controlled in any sense.

One of the interesting characteristics of the molecularly dispersed system investigated here is, therefore, the controllability of the "dispersoid" nature such as nonlinear molecule concentration, dispersion size and molecular orientation. In this article, we will discuss details regarding MNA dispersed PMMA thin films, in which the femtosecond laser pulse compression has been reported, and also of the MNA dispersed cellophane films. In addition to these experiments carried out under ambient pressure, newly developed pressure tuning spectroscopy(PTS),[8] a very potential method to investigate the interaction between the dispersoid and matrix, has been performed, because it can exert physical perturbation on the structure of a compound without changing the molecular composition or molecular system.

## Experimental

Two kinds of MNA doped thin films, PMMA(MNA/PMMA) and cellophane (MNA/cellophane), were mainly investigated in the present work. The MNA/PMMA film was doped by using a vacuum hot-press method at about 150℃ and the MNA/cellophane film was doped by the immersion in acetone solution for 4-5 hrs. The MNA for doping was purified with sublimation in vacuum. The size of doped MNA molecules, probably microscopically aggregated in the films, was inspected by using X-ray diffraction and scanning electron microscopy(SEM). Absorption spectroscopy over visible and ultraviolet wavelength regions was carried out on a commercial spectrophotometer. Second (SHG) and third(THG) harmonics generation excited by 1.06 μm and 1.89 μm fundamental laser light, respectively, was observed with a monochromator/photomultiplier system. In high-pressure experiments, a hand-made microscope, being capable of visible and ultraviolet absorption spectroscopy, was coupled with a commercial spectrophotometer via optical fiber optics.[9]

## Results and discussion

### Condensed states in the densely doped MNA/PMMA film

Condensed states in the densely doped MNA/PMMA film have been investigated by means of optical absorption spectroscopy and X-ray diffraction. Absorption $\lambda_{max}$ and fwhm of the dispersed MNA and MNA solution were measured on a spectrophotometer as summarized in Table 1 and Table 2. Absorption $\lambda_{max}$ of MNA/PMMA showed an intermediate value between those of the crystal MNA and the MNA solution in non-hydroxylic solvents of low static dielectric constants( $\varepsilon$ ),

| MNA／Matrix | $\varepsilon$ matrix | $\lambda$ max [ nm ] | fwhm [$cm^{-1}$] | SHG／THG | Remarks |
|---|---|---|---|---|---|
| Crystal a) | --- | 385 | --- | ○／○ | KBr pellet |
| PMMA | 3.6 | | | | Non-Hydroxy |
| ~ 6 M | | 367 | 8236 | ×／○ | |
| $8.2\times10^{-2}$ M | | 366 | 5867 | --- | |
| ~ $1\times10^{-3}$ M | | 367 | 4877 | --- | |
| Cellophane | 4.3-4.5 b) | | | | Hydroxy |
| Melt-doped c) | | 385 | 5374 | ×／○ | |
| 0.26 M | | 389 | 5347 | ×／○ | |
| $2.7\times10^{-2}$ M | | 386 | 4978 | --- | |
| $2.9\times10^{-3}$ M | | 383 | 4417 | --- | |

Table 1 Matrix dependence of the optical properties of MNA crystal, dispersed MNA/PMMA films and dispersed MNA/cellophane films. a) MNA concentration of 2.5x10-4 mol in KBr pellet; b) at a frequency of 1-10 MHz; c) doped with a melted liquid of MNA in vacuum.

| Solvent (concentration; $\times10^{-4}$ M) | $\varepsilon$ solvent a) | $\lambda$ max [ nm ] | fwhm [$cm^{-1}$] | Remarks |
|---|---|---|---|---|
| Benzene (1.0) | 2.3 | 348 | 4879 | N-Hydroxy |
| Xylene (---) | 2.4 | 345 | 4792 | N-Hydroxy |
| Acetone (0.7) | 21.2 | 369 | 4534 | N-Hydroxy |
| EtOH (2.2) | 24.2 | 374 | 5460 | Hydroxy |
| H20 (1.7) | 78.5 | 384 | 6121 | Hydroxy |

Table 2 Solvent dependence of the optical properties of MNA. a) Akhadov,Y.Y. Dielectric Properties of Binary Solutions, Pergamon: Oxford, 1980; Chap. II.

and it was almost constant with the variation in the concentration of MNA which was intentionally varied over more than 3 orders of magnitude from 6 mol/l to $1x10^{-3}$ mol/l. The 6 mol/l MNA/PMMA film contains MNA doped to PMMA as dense as about 33 mol%, but absorption $\lambda_{max}$ was far different from that of the crystal. For the purpose of analyzing the matrix effects on absorption $\lambda_{max}$, the MNA solution was spectroscopically studied for several kinds of solvents with different $\varepsilon$.[10] It is essential in nature to differentiate hydroxylic from non-hydroxylic solvents. PMMA as a solvent is considered to be a non-hydroxylic one with a low $\varepsilon$ value. Absorption $\lambda_{max}$ showed a monotonous correlation with $\varepsilon$ of the solvents. Absorption $\lambda_{max}$ of MNA/PMMA differs from that of MNA in a benzene solution which has an $\varepsilon$ similar to PMMA. Though absorption $\lambda_{max}$ of MNA/PMMA was almost constant over a wide MNA concentration range, fwhm varied as the MNA concentration increases. Since the X-ray diffraction pattern of the dense film suggests that it dose not include a macroscopic MNA crystal structure(Figure 1), which is reasonably deduced from the result of HG measurements, the condensed state of the MNA/PMMA film is readily concluded to be the state that does not have a mono-molecular dispersion but some kinds of amorphous-like condensation stabilized with a strong coupling between MNA and PMMA.

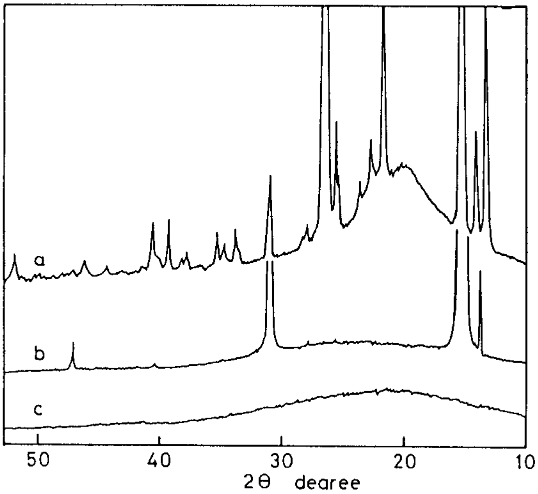

Fig. 1 X-ray diffraction for MNA powder crystal(a), partly recrystallized MNA/PMMA film(~8.5 M)(b) and transparent MNA/PMMA film(~7 M)(c).

### Condensed states in the densely doped MNA/cellophane film

Condensed states in the doped MNA/cellophane have also been investigated by means of optical absorption spectroscopy and X-ray diffraction spectroscopy. While the dispersed size of MNA in the cellophane film has not measured by any methods, the diameters of dispersoid should be of the order of several tens of nanometers which are too small to be detected by the X-ray diffraction method, because in cellophane films, there are many micro-pores whose diameter is distributed between 5 and 13 nm[11] and transparency and clearness of the film are kept after doping. This situation is as follows. At the first doping stage, the organic dyes condense at the pores by physical adsorption without inducing a change in film structure. At the second stage, if possible under the available conditions, the organic dyes condense in the amorphous regions of the film with increasing the thickness. Since, in the case of doping by a nonaqueous solvent or melt doping, only the first doping stage occurs, the doped dye is thought to condense in the pore space and fill them up. This presumption is supported by the fact that absorption $\lambda_{max}$ of MNA/cellophane has the same value as the crystal one(Table 1), implying that a crystal-like condensation of MNA in the cellophane film though its size is of the nanometer order. The inhomogeneous broadening indicated in the fwhm increase in the denser MNA/cellophane film is also recognized but less pronounced than that for the MNA/PMMA film. The narrowing of the fwhm by about 100 $cm^{-1}$ under a decreased temperature at 114 K was observed, contrarily to the case of the MNA/PMMA film(about 131 $cm^{-1}$ broadening at 114 K), and this also supports the crystal-like condensation in the MNA/cellophane film. Such narrowing results from the situation that, as in the usual molecular crystals, thermally activated vibrational sublevels in the ground-state molecule are quenched by the reduction in temperature.

### Pressure effects on the doped film

As for the concentration dependence of MNA in the PMMA film and the cellophane film, absorption $\lambda_{max}$ remains almost constant, and fwhm become larger as the concentration increases. In contrast to these, in MNA/PMMA and MNA/cellophane, both $\lambda_{max}$ and fwhm are changed differently as the pressure increases. In both films, the longer wavelengths shift of absorption $\lambda_{max}$ larger than 20 nm may result from intramolecular effects of the MNA molecule. While condensed states of the MNA molecules in the PMMA film are different from those in the cellophane film, a pressure dependence of absorption $\lambda_{max}$ in the MNA/PMMA is identical with that in the MNA /cellophane. If $\lambda_{max}$ is controlled mainly by the interactions between the molecule and matrix, the pressure dependence should be different between them. Therefore the application of the pressure on the MNA dispersed matrices causing hydrostatic pressure on the MNA molecule is supposed to bring about a stabilization of the ground states due to distortion of methyl substituents in the MNA molecules or a stabilization of lowest excited states due to a formation of MNA dimeric pairing.

Though a precise discussion on the absolute value of fwhm is difficult because of the limitations of the high pressure measurement apparatus, essential phenomena of the pressure dependence are final increases in fwhm which are minimum at lower pressure. fwhm, as previously stated, exhibits inhomogeneous broadening which may come from distributions of the microscopic environment of the molecule in matrices. Since fwhm is increased in denser films and, also, at very high pressures, fwhm will be affected by interactions between the MNA and matrix. Also the minimum in the pressure dependence is supposed to result from possible re-orientations of the MNA molecules or MNA aggregates in the matrix towards lower dispersion free energies. Of course, this tendency stops at the 1.0 GPa level, and, above it, the rigid matrix hardening effect increases the environmental fluctuation potential and, therefore, fwhm.

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