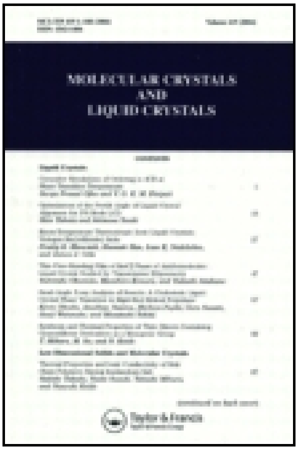

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Photoisomeric-Chromophore-Based Nonlinear Optical Response for Four Wave Mixing

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Photoisomeric-Chromophore-Based Nonlinear Optical Response for Four Wave Mixing

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We theoretically and experimentally investigated the photoisomerization of azo chromophores and the resulting nonlinear optical response of transmission and four wave mixing through the two-energy-level model. The rising time constant of the transmission obtained by the model gave good agreement with that of the wave-mixing signal. In addition, we tried to improve the time response by using photoactive polymers ionic-bonded with azo chromophores.

Keywords: azo chromophore; photoisomerization; wave mixing

INTRODUCTION

Azo chromophores have drawn much attention because a light induces their photoisomerization, which is potentially useful for photorefractive wave mixing[1], holographic data storage[2], and information processing[3]. The chromophore compounds have generally a high optical nonlinearity and/or a high polarization sensitivity.

In this paper we report the photoisomeric nonlinear optical response of a methyl-orange (MO)-doped polyvinyl alcohol (PVA) film and a MO-ionic-bonded polyallyl amine (PAA) film through a simple theoretical prediction of the two-energy-level system and experimental investigations.

Photoisomeric Time Response

It is well known that the photoactive chromophores of azo groups undergo reversible trans-cis photoisomerization, and this allows the photoactive units. We used azobenzene derivatives and polymer matrices as a sample. In addition to the change in optical absorption characteristics, the trans and cis isomers have different molecular shapes. These induced geometric changes in the photoactive groups may invoke variations in the optical properties of the matrix material. If any mixture of the two isomers is irradiated with visible light, the composition changes with time, approaching asymptotically the photostationary composition. By using the two-energy-level model proposed in Ref.[4] the temporal transmission of a film with thickness L can be written

$$T = \exp\left\{-\left[\sigma_T N_0 + (\sigma_C - \sigma_T)\frac{B}{A}(1 - \exp(-At))\right]L\right\}, \tag{1}$$

where

$$A = \frac{I}{\hbar\omega}(\sigma_T\phi_T + \sigma_C\phi_C) + K,$$

$$B = \frac{I}{\hbar\omega}\sigma_T\phi_T N_0.$$

ϕ_T and ϕ_C are the quantum yields from the trans to cis isomer and from the cis to trans isomer respectively, σ_T and σ_C are the respective absorption cross sections for two isomers respectively, K is the thermal reaction constant from the cis to trans isomer, and I is the pump beam intensity. Suppose that the azo chromophores stay in the biradical excited energy state only in a short time, we can approximate the total number of two isomers per unit volume as constant N_0. The rising time constant of the photoinduced transmission after the intense beam exposure is given by

$$\tau = \frac{1}{\frac{I}{\hbar\omega}(\sigma_T\phi_T + \sigma_C\phi_C) + K}. \tag{2}$$

Suppose that the response of the nonlinear transmission in the resonant wavelength region of the photopolymer mainly contributes to that of the four wave mixing (FWM) signal, the rising time constant of the FWM is calculated by taking double logarithms of the temporal development of the signal.

Time Response for FWM in Guest-Host Polymers

We focus attention on the time response for the FWM in a guest-host polymer film. The MO-doped PVA film with 100 μm thickness was used as the photoactive guest-host-type polymer. Fig. 1 shows the pump beam intensity dependence of the rising time constant of the nonlinear transmission and the FWM. The time constant of the transmission was estimated by fitting the temporal data to Eq. (1). Also, the time constant of the FWM signal was calculated by taking double logarithms of the signals. This experiment was performed by Ar^+ laser (λ=514.5 nm) for the film of the absorbance α_0L = 2.1, where α_0 is the linear absorption coefficient. As predicted in Eq. (2) the increase in the pump intensity resulted in the linear decrease in the time constant. The time constant of the FWM gave good agreement with that of the nonlinear transmission through the simple theoretical prediction of two-energy-level system. This result indicates that the photoisomeric absorptive nonlinear response mainly contributes to the mechanisms of the FWM.

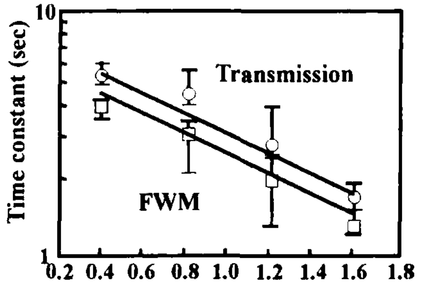

FIGURE 1 Pump beam intensity dependence of rising time constant.

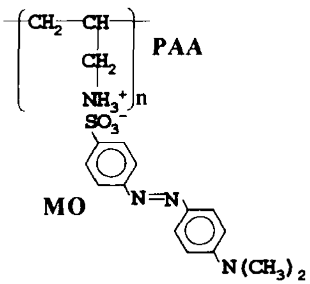

FIGURE 2 Chemical structures of MO/PAA.

Time Response for FWM in Chromophore-Ionic-Bonded Polymers

The chemical structure of the MO/PAA polymer composite is shown in Fig. 2. In this polymer system the chromophore is weakly combined with a

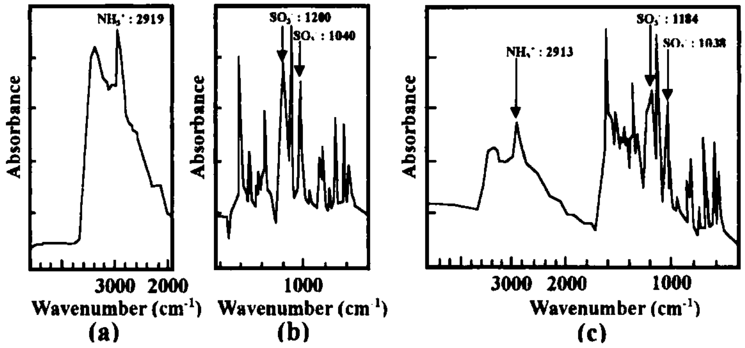

FIGURE 3 Infrared absorption spectra of (a)PAA, (b) MO, and (c) MO/PAA.

main chain by an ionic bond. The semi-fixed structure of chromophores allows the wave-mixing signal to make a quick response. In order to investigate the structure of the chromophore-ionic-bonded polymer we measured the infrared absorption spectrum of the MO/PAA film. The respective spectra of PAA and MO are illustrated in Figs. 3(a) and 3(b) respectively. The well known characteristic absorption peaks are 2919 cm^{-1} of NH_3^+ in PAA, 1040 and 1200 cm^{-1} of SO_3^- in MO. Three characteristic peaks shifted to the small wavenumber in the MO/PAA film (see Fig. 3(c)). This result proved that MO as a side chain was ionic-bonded with PAA as a main chain.

We measured the rising time constant of the FWM signal in the MO/PAA film. The time constant of the signal, for example, was 0.35 sec for $I = 0.4$ W/cm^2 and the absorbance $\alpha_0 L = 2.1$ at $\lambda = 514.5$ nm. The improvement in the time response by more than one order of magnitude was obtained by weakly combing the chromophores with main chains.

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