Third–Order Nonlinear Optical Properties of Dye-Doped Polymer Thin Films

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Abstract

Third–Order Nonlinear Optical Properties of Dye-doped Polymer films Measure by quick and simple Method. This simple method is shown to provide quick measurements of the $\chi^{(3)}_{1133}$ component of the third-order optical susceptibility. The measured quadratic electro-optic coefficient of 7.0 wt. % (30 mol %) of a dicyanovinyl azo dye in PMMA [poly (methyl methacrylate)] is 4.2×10^{-21} m^2/V^2, which corresponds to a direct current Keer coefficient of 1.4×10^{-11} esu. Azo dye doped exhibit excellent transmission spectra in visible resion, which shows that the materials is promising for integrated optics.

Key words: Dye-doped polymer, Third order susceptibility, Quick and simple method

1. Introduction

During the last decades, research interests have been focused on electro-optical materials [1-3]. Nevertheless, because of the heavy and expensive growth techniques of these inorganic compounds, research moved towards polymeric materials. Indeed, this family has the advantage to the suitable to low cost molecular engineering processes very useful for specific applications. Another advantage of polymers is the possibility to achieve reliable doped thin films with customizable properties. It has been also demonstrated that by suitable doping, stable photoinduced optical behaviors (photorefractive effects, birefringence, dichroism, holography, etc.) can be produced and used to design new generation of optically controlled devices. Doped polymeric materials offer high optical quality

and potentially large bulk nonlinear susceptibilities if the molecular hyperpolarizability of the dopant is large. A copolymer of azo-dye-substituted acrylic monomer and methyl methacrylate has been recently shown to have a third harmonic susceptibility of $\chi^{(3)}$ ==1.25 × 10^{-12} esu[4]. Here we present a simple experimental method that is well suited for thin film measurements. Results for various dyes are presented to show that electro-optic methods can be used to measure third order susceptibilities of doped thin films with fast response times because molecular motion is hindered by the host[5] and thus reduces the influence of these slower processes on the measurements.

2. Experimental

A film is placed in one arm of a Mach-Zehnder interferometer (film plane perpendicular to the laser beam) and the relative phase between the two arms is controlled with a rotating glass slide in the other arm. The measurement is made in two steps. First, the intensity of the laser light coming out of the interferometer is measured as a function of the glass slide angle. A chopper is used with a lock-in amplifier to reduce noise. Second, the phase in the sample arm is modulated by applying an electric field to the film sample along the direction of the laser beam. The transparent indium tin oxide films are used for electrodes. The signal at the modulation frequency and at twice the modulating frequency is recorded as a function of the glass plate angle.

This scanning technique, were both the laser power and the modulation intensity are measured as a function of phase difference between the two arms, determines the absolute values of the second and third order susceptibilities without tuning the interferometer and without the need for a reference material. It is similar to other scanning techniques where the phase is adjusted by scanning over the light frequency out of a Fabry-Perot interferometer and to nonscanning techniques that use nulling with a known material [6]. Because the material is prepared to be

centrosymmetric, there is no bulk second-order susceptibility and the light is only modulated at twice the frequency of the applied voltage. The real part of the quadratic electro-optic coefficient, s_{1133}, can be calculated from the interferograms made in the two steps:

$$s_{1133} = -\frac{\lambda d}{2\pi n^3 V^2_{rms}}(\frac{I^2_{2\Omega}}{2I^2_{sig}} - \frac{I^4_{\Omega}}{I^4_{sig}})^{1/2} \qquad (1)$$

where λ is the laser wavelength, d the film thickness, n is the refractive index, V_{rms} is the root mean square (rms) modulating voltage, I_{sig} is the interferogram amplitude of the signal at the modulating frequency (Fig.1). Note that the second order susceptibility of the material can result in a contribution to the modulation amplitude at twice the modulating frequency. This effect is subtracted out by the second term in brackets in equation 1. There are several mechanisms that can lead to an electric field dependence of the refractive index, or physical dimensions of a sample. Both effects leads to a change in the optical path length through the sample. The possible mechanisms contributing to measurements of the third order susceptibility are electronic, orientationally induced second-order effects, electrode attraction, electrostriction, trapped charge movement and heating. Considerations of these mechanisms show that the sum of the third order susceptibility contributions from heating, trapped charge movement, electrostriction effects is nearly identical in doped and undoped materials. These slower effects can thus be accounted for by comparing the nonlinear optical properties of the doped and undoped polymer host.

3. Result and Discussion

The transmission spectra of the azo dye-doped is shown in Fig. 1. It is clear from the figure that films have good transmittance at 633 nm. The change in refractive index with applied field from molecular reorientation gives a quadratic electro-optic coefficient.

$$J_{1133} = -\frac{16}{105}\pi N\alpha*(-\Omega;\Omega) \times \frac{\alpha*(-\omega;\omega)}{k_0}(7+5A_2-12A_4) \tag{2}$$

where N is the number density of dopant, $\alpha*$ is the local field corrected molecular susceptibility of the dopant, Ω and ω are the modulating and optical frequencies; respectively, k_0 is the orientational elastic constant of the dopant molecule in the polymer matrix, A_2 and A_4 the two lowest order parameters that give the first two axial moments of the dopant orientation function[7].

The application of the modulating field can also break the centrosymmetry of the sample. The change in the refractive index of the bulk is then the result of a linear electro-optic effect in the instantaneously poled film. We refer to this contribution as the orientationally induced second-order effects. The quadratic electro-optic coefficient from this source in Gaussian units is

$$J_{1133} = 4\pi\frac{N\beta*_{zzz}\mu*}{35k_0 n_{11}}(14-50A_2+36A_4) \tag{3}$$

where $\beta*$ is the molecular local field corrected second order optical susceptibility, n_{11} is the refractive index in the film plane, and $\mu*$ is the local field corrected dipole moment.

The dopant molecules in this study are the azo dye disperse red 1 (DR1), the dieyanovinyl azo dye (DCV), and the nitrofuran dye (NFAI). The DCV data are shown in Fig.2. The bottom curve shows the single at the detector for pure poly (methyl methaacrylate) (PMMA) at twice the modulating frequency (Ω=4 kHz) with V_{rms} = 90 V. The polymer signal is in the noise showing that the polymer contribution is small. The middle curve shows the signal for PMMA doped with DCV (2.5 mol %) at twice the modulation frequency and the upper curve maps the interferometer output with no modulation. With a modulation voltage of V_{rms} = 47.98 V (d=3.9 $\times 10^{-6}$ m, n=1.50, λ=633 nm), the quadratic electro-optic coefficient is s_{1133} =4.2 $\times 10^{-21}$ m^2/V^2 which corresponds to a de Kerr coefficient of J = 1.4 $\times 10^{-21}$ esu. The measured quadratic electro-optic constants of the dyes

are shown in Table 1. The third-order susceptibility is calculated from the Kerr coefficient and is $\chi^{(3)}_{1133}=1.3(\pm 0.5)\times 10^{-13}$ m^2/V^{2}esu giving an electronic susceptibility of $\chi^{el}_{1133}=1.9(\pm 0.7)\times 10^{-13}$ esu for a concentration of 2.5 mol % (7.5 wt. %). The electronic susceptibility of a 26 mol % DR1 azo dye material was determined to be $\chi^{(3)}=1.26\times 10^{-12}$ esu from third harmonic generation. Our values agrees with this value if the linear concentration dependence of the third order susceptibility is taken into account.

4. Conclusion

We have shown that quadratic electro-optic modulation can be used to estimate the electronic third order optical susceptibility of thin films. Quadratic electro-optic modulation was demonstrated in isotropically doped polymers for three organic dyes and a detailed analysis of the third-order mechanisms shows that for DR1, the measured susceptibility is mostly electronic. This simple and quick interferometric technique can be used to determine the third order susceptibilities of any doped polymer system.

References

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Table 1. Nonlinear optical properties of dye-doped films at $\lambda=633$nm.

Dopant	Concentration (wt. %)	λ_{max} (nm)	S_{1133} ($10^{-21}m^2/V^2$)	J (10^{-12} esu)
DR1	7.0	471	1.0($\pm$0.1)	3.15($\pm$0.25)
DCV	7.0	499	4.35($\pm$0.5)	13.5($\pm$0.1)
NFAI	9.5	464	1.25($\pm$0.1)	3.8(($\pm$0.45)

Figure Caption

1. Transmission spectra (a) DR1, (b) DCV and (c) NFAI.

2. Bottom curve shows electro-optic modulation intensity of pure PMMA and the middle curve shows electro-optic modulation of DSV-doped PMMA at twice the modulating voltage frequency. The upper curve shows the interferometer output as a function of glass plate angle with no modulation voltage.
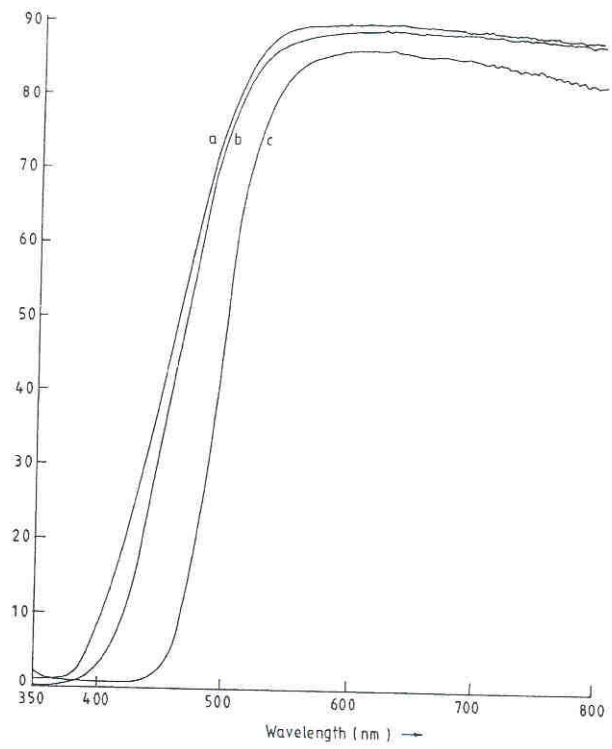
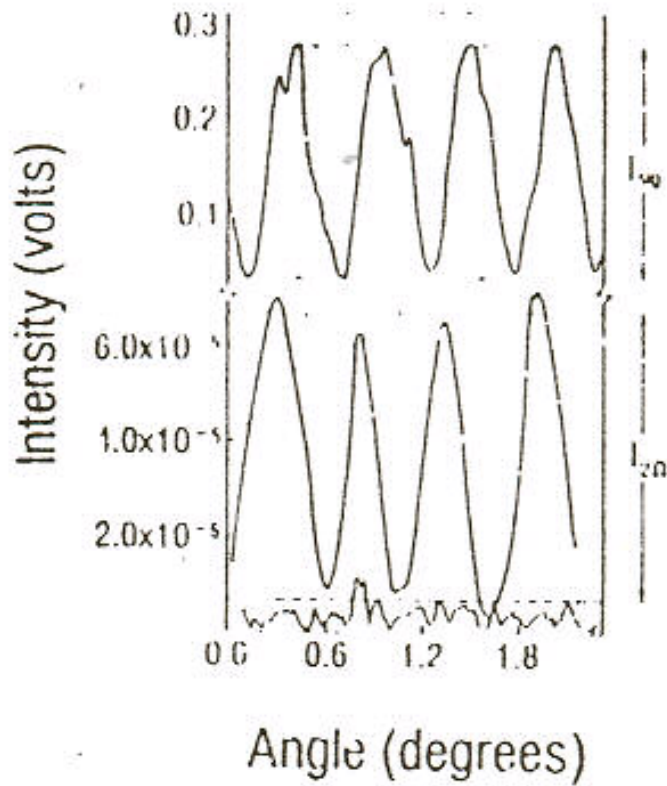Fig.1. Transmission spectra (a) DR1, (b) DCV and (c) NFAI

Fig. 2 Bottom curve shows electro-optic modulation intensity of pure PMMA and the middle curve shows electro-optic modulation of DSV-doped PMMA at twice the modulating voltage frequency. The upper curve shows the interferometer output as a function of glass plate angle with no modulation voltage.