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STABILITY OF ELECTRIC FIELD INDUCED ORDERING IN A UV-CURABLE POLYMER SYSTEM

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Abstract The stability of the electric field induced ordering in a UV-curable polymer system is studied by probing the second harmonic generation (SHG) process. The field induced SHG intensities from the polymer film are measured as a function of the azimuthal angle for rotation at oblique incidence in various polarization geometries. The symmetry group of the polymer film under the electric field is unambiguously determined, and the effective nonlinear optical (NLO) susceptibilities are obtained from the SHG intensity profiles. The field and temperature dependence of the NLO susceptibilities are described in terms of the third-order optical nonlinearity.

INTRODUCTION

Much progress in the development of organic materials with high nonlinear optical (NLO) properties have been made over recent years for their potential use in electro-optic and photonic devices such as optical switches, light modulators, and logic gates.[1–3] These materials possess several important features such as large optical nonlinearity, high damage threshold, fast temporal response, and high transparency over a wide range of wavelength. Moreover, the organic materials can be processed easily and efficiently into thin films by a variety of techniques. Particularly, electrically poled polymers show promising NLO efficiencies as well as much improved thermal stability of the nonlinearity.[4,5]

Although the NLO properties of the dopant dye in the host polymer matrix

have been extensively studied,[3–5] the optical nonlinearity of the host polymer itself and its stability have not been fully explored so far. In this work, we present experimental results for the stability of the field induced ordering in UV-curable polymers, acquired during the field poling process, by the second harmonic generation (SHG) measurements. These polymers can be used as a host matrix in various guest-host systems.[6] It is found that the NLO response of the polymer comes mainly from the third-order nonlinearity. Moreover, the field induced SHG is nearly independent of temperature.

EXPERIMENTAL

The material being studied was a commercial UV-curable epoxy (curable wavelength: 320–400 nm), NOA 60, obtained from Norland Corp. The sample cell consists of two glass substrates with transparent electrodes on the inner surfaces so that an external electric field is applied to it. The cell thickness is nominally 10 μm. The polymer was filled into the cell by capillary action before UV curing. The curing of the polymer was carried out by a 100 W mercury lamp of 365 nm at room temperature.

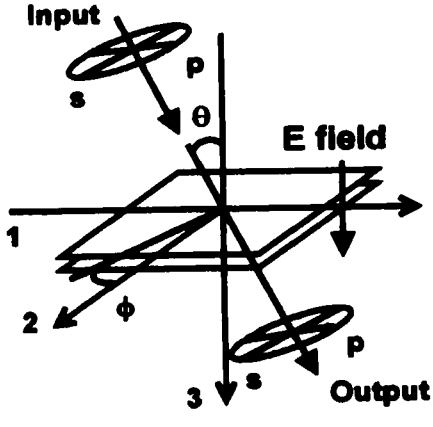

FIGURE 1 (a) The experimental geometry; Input and output represent the fundamental and SHG beam, respectively. (p and s are the polarizations). An external electric field is applied along the 3 axis.

The experimental geometry used is shown in Fig. 1, where θ is the incident angle and ϕ the azimuthal angle for rotation with respect to the surface normal. The SHG measurements were performed using a fundamental beam of a Q-switched Nd:YAG laser (1064 nm, 10 ns, and 10 mJ/pulse). A single crystal of a quartz plate was used as a reference (d_{11} = 0.49 pm/V)[7] to determine the relevant NLO coefficients of the polymer.

RESULTS AND DISCUSSION

The application of an external electric field generates a polar axis in the polymer film. This axis contains essentially an infinite-fold rotational symmetry with an infinite number of mirror planes (∞mm or $C_{\infty,V}$). The SHG intensity, $I(2\omega)$, from the film is proportional to the square of the second-order polarization, $P^2(2\omega)$ for the fundamental input $E(\omega)$. When the Kleinman symmetry is taken and the induced birefringence in the film is ignored, the expression for $P(2\omega)$ in terms of θ and ϕ for given polarizations, s and p, can be written as

$$\begin{aligned} P_{pp}(2\omega) &= \Big[2d_{33}\sin^2\theta_\omega \sin\theta_{2\omega} + 2d_{31}\cos\theta_\omega \\ &\qquad \times (2\cos\theta_{2\omega}\sin\theta_\omega + \cos\theta_\omega \sin\theta_{2\omega})\Big]\ E_p^2(\omega)\ , \qquad (1) \\ P_{sp}(2\omega) &= [2d_{31}\sin\theta_{2\omega}]\ E_p^2(\omega)\ , \quad P_{ps}(2\omega) = 0\ , \quad P_{ss}(2\omega) = 0. \end{aligned}$$

Here E_p's are the effective components of the fundamental field, d_{ij}'s the nonzero second-order NLO coefficients for the $C_{\infty,V}$ symmetry group, and $\theta_\omega = \sin^{-1}(\theta/n_\omega)$. The subscripts, p and s, represent the polarizations of the fundamental and SHG beam. As is clear in Eq. (1), the resultant SHG intensities are independent of the azimuthal angle for rotation ϕ, so that it is simple to deduce information about the NLO coefficients of the film.

We first measure the SHG intensity from a x-cut quartz plate, which belongs to the D_3 symmetry group, as a function of ϕ to see the validity of our theoretical predictions. As shown in Fig. 2(a), the predictions are in good agreement with the experimental data. We now discuss the SHG intensity from the NOA 60 polymer

film. Fig. 2 (b) shows the ϕ dependence of the SHG intensities for two different polarizations at the applied field $E = 10$ V/μm. As expected from Eq. (1), no s-polarized SHG signal was detected, and all p-polarized SHG intensities are observed. Moreover, the p-polarized intensities indicate that the polymer film has indeed the $C_{\infty,V}$ symmetry. Using Eq. (1), the second-order NLO coefficients d_{ij}'s are readily determined as $d_{33} = 2.81 \times 10^{-2}$ pm/V and $d_{31} = 1.02 \times 10^{-2}$ pm/V. Note that d_{33} is the dominant tensor element and $d_{33}/d_{31} = 2.75$.

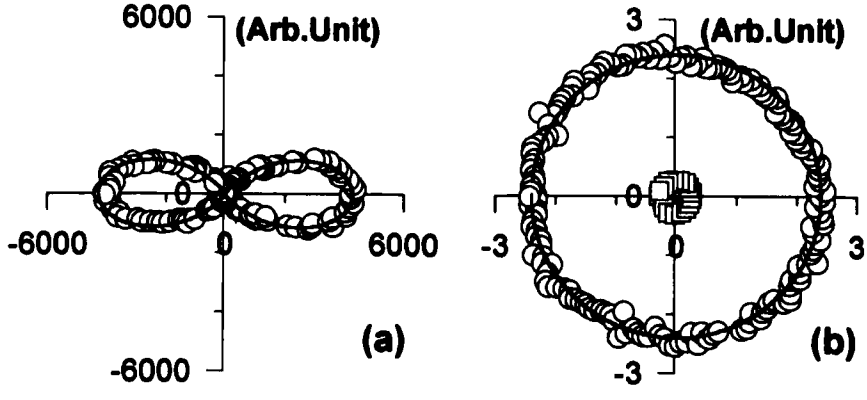

FIGURE 2 The p-polarized SHG intensity profiles as a function of ϕ at $\theta = 50°$; (a) a x-cut quartz crystal and (b) NOA 60 polymer film. The circles and squares represent $I_{pp}(2\omega)$ and $I_{sp}(2\omega)$, respectively. The solid lines are the least-square fits of the data to Eq. (1).

Although the optical nonlinearity is relatively small, the polymer itself (with no NLO dopant) experiences the SHG process. For describing the physical mechanism for the SHG from the polymer, we measured $I_{pp}(2\omega)$ as a function of the electric field E and temperature. The SHG intensity is proportional to E^2, which suggests that the third-order optical nonlinearity plays an essential role in the NLO process of the polymer film. The effective second-order coefficient is then expressed in terms of a linear coupling between the third-order nonlinearity, $\chi^{(3)}$, and a static field, $E(0)$, i.e., $d_{ijk} = \chi^{(3)}_{ijkl}(-2\omega;\omega,\omega,0)E_l(0)$. This term is exactly what contributes to the SHG data in Fig. 2(a). Defining a microscopic hyperpolarizability γ by

$\chi^{(3)}/NF$ with N the density of molecules and F a proper local field factor,[2] the hyperpolarizability γ is written as[8] $\gamma = \gamma_{el} + \mu\beta/5kT$, where γ_{el} represents the electronic contribution, β the vector part of the quadratic hyperpolarizability tensor, μ the permanent dipole moment, k the Boltzmann constant, and T the temperature. Note that the second term in the above expression for γ is related to the partial orientation of the permanent dipole moment in a static electric field.

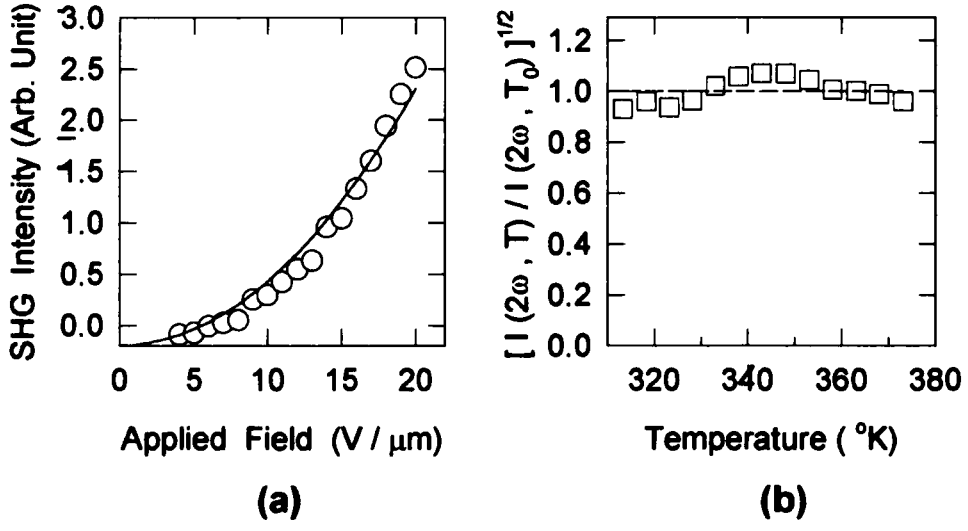

FIGURE 3 (a) The electric field dependence of $I_{pp}(2\omega)$. (b) The temperature dependence of $\sqrt{I_{pp}(2\omega)}$. $T_0 = 293°$ K. The solid lines are the least-square fits.

In our case, the electronic contribution γ_{el} may be more significant than the orientational one since no NLO dopant molecules with high β and μ are introduced into the system. In terms of the hyperpolarizability γ described above, the expression for the SHG intensity is given by $\sqrt{I(2\omega)} \propto NF(\gamma_{el} + \beta\mu/5kT)\ E(0)$.

Fig. 3 (b) shows the temperature dependence of $\sqrt{I(2\omega)}$ for the polymer film. As is evident from Fig. 3, $\sqrt{I(2\omega)}$ remains nearly constant, independent of the temperature. This means that the orientational contribution to the SHG intensity is negligible. It might be then concluded that the SHG process in the UV-curable polymer, NOA 60, comes mostly from the cubic hyperpolarizability. From the effec-

tive values of the second-order NLO coefficients, the magnitude of $\chi^{(3)}(-2\omega;\omega,\omega,0)$ is estimated; $\chi^{(3)}_{3333} = 5.51 \times 10^2$ pm^2/V^2 and $\chi^{(3)}_{3311} = 2.01 \times 10^2$ pm^2/V^2. These values are on the same order as those for typical NLO polymers[2] ($10^2 \sim 10^3$ pm^2/V^2). Interestingly, the ratio of $\chi^{(3)}_{3333}/\chi^{(3)}_{3311} = 2.75$ is in good agreement with the predicted ratio of 3 in the isotropic model.[2,6]

CONCLUDING REMARKS

We have studied the stability of the field induced ordering in a UV-curable polymer system by the SHG processs. It was found that the polymer film, poled by an external electric field E, exhibits an infinite rotation symmetry. The SHG intensity is propotinal to E^2, and it is nearly independent of temperature. The NLO response of the polymer film is described in terms of the third-order optical nonlinearity which couples linearly with the dc electric field.

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