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Second Harmonic Generation by Polymer Dispersed Liquid Crystal Films

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In this paper, we report measurements of optical second harmonic generation by polymer dispersed liquid crystal (PDLC) films. These materials consist of micron sized liquid crystal droplets dispersed in a polymer matrix; they are formed by the phase separation of a homogeneous prepolymer-liquid crystal mixture. Using a Q-switched Nd:YAG laser, we have observed a second harmonic signal with increasing intensity during the phase separation process. By applying a dc field to the fully cured sample which reorients the liquid crystal in the inclusions, we were able to modulate the intensity of this second harmonic signal. We propose that the symmetry breaking field responsible for second harmonic generation is the dielectric constant gradient caused by the inhomogeneity of the PDLC film. Although interesting in itself, the process of dielectric constant gradient induced second harmonic generation may also be useful in studying the time evolution of the structure factor in systems undergoing phase separation.

INTRODUCTION

Polymer Dispersed Liquid Crystal materials consist of liquid crystal droplets dispersed in a polymer binder. PDLC films are formed by phase separation of an initially homogeneous mixture of prepolymer and, in our case, a nematic liquid crystal. As the polymerization proceeds, the liquid crystal phase separates to eventually form approximately micron sized droplets which are nearly spherical in shape. The liquid crystal in the inclusions can be oriented by externally applied electric or magnetic fields. If the ordinary refractive index of the liquid crystal is matched to that of the polymer, then the films can be switched from a scattering to a clear state.[1] Because of their usefulness in a variety of display applications, these materials have attracted a great deal of attention recently.

Optical second harmonic generation is forbidden[2] in materials with inversion symmetry, hence SHG is not observed in bulk nematic liquid crystals and isotropic polymers. The presence of sufaces and interfaces, however, breaks inversion symmetry, and hence SHG is allowed at interfaces between centrosymmetric materials. Such surface induced second harmonic generation (SSHG) has been shown to be a powerful probe of surfaces and interfaces.[3]

PDLC materials are interesting candidate materials for SSHG for a number of reasons. First, they provide an extensive interface between the polymer and the

liquid crystal; the surface-to-volume ratio is inversely proportional to the droplet radius, and can be made very large. Second, the refractive index difference across the interface can be varied by applying an external field. Finally, as an initially homogeneous prepolymer-liquid crystal mixture undergoes phase separation, concentration gradients evolve in time to form interfaces. Consequently, second harmonic generation can give information about the kinetics of the phase separation process.

EXPERIMENTAL RESULTS AND DISCUSSION

The schematic of the experimental setup is shown in Figure 1. The fundamental output at 1.06 μm from a Q-switched Nd:YAG laser was normally incident and slightly focused onto the sample to give a beam waist of approximately 0.5 mm.[2] The transmitted SH signal at 532 nm was detected by a photomultiplier (PMT).

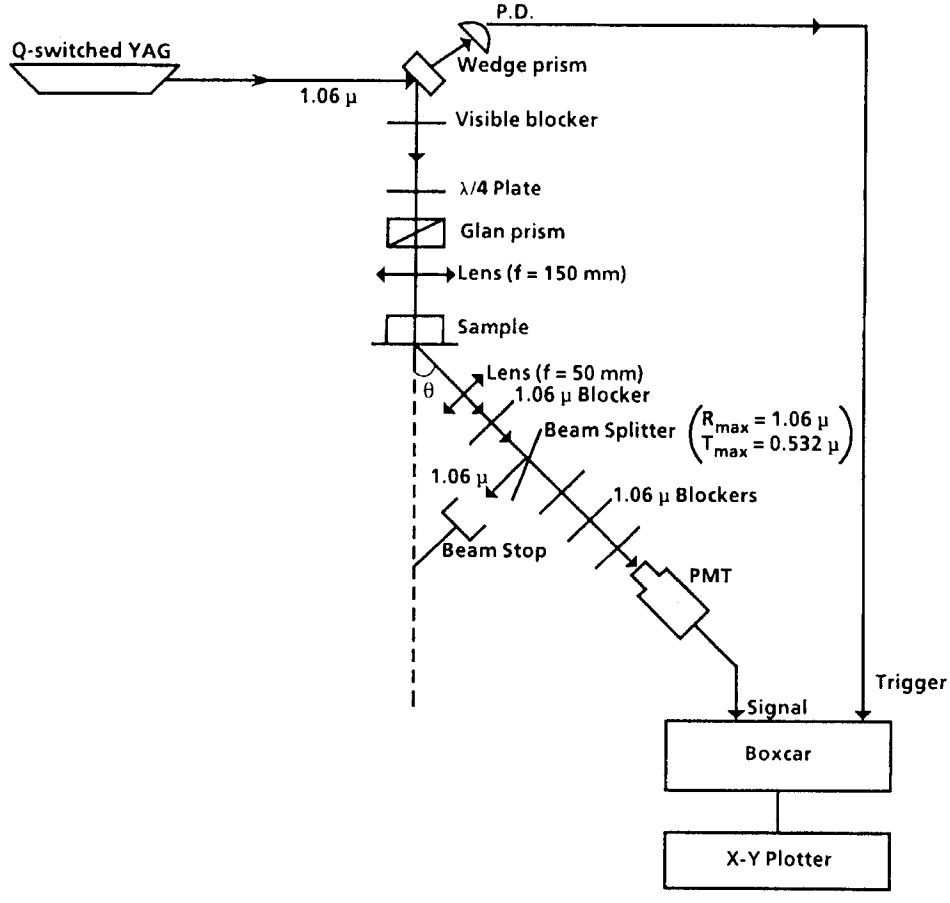

FIGURE 1 Experimental setup for second harmonic generation measurement.

The signal from the PMT was sent to a boxcar averager followed by a X-Y plotter. The energy of the incident 8 ns pulses was 0.5 mJ; no damage to the sample could be observed at this incident intensity. The detection system is mounted on a rotating stage in order to allow determination of the angular distribution of the SH signal.

The sample was prepared filling a 30 μm thick glass cell with a homogeneous mixture of the liquid crystal E7, the prepolymer Epon 828 and the curing agent Capcure 3-800. The composition was equal amounts of the three components by weight. The cell windows were coated with a transparent conducting ITO layer to allow the application of a voltage across the cell.

The second harmonic signal observed during the phase separation process is shown in Figure 2. The time origin is chosen to be nine hours after the sample preparation; the sample was cured at room-temperature. As can be seen in Figure 2, the SH signal becomes detectable only after nine hours and forty minutes. We expect, from linear light scattering results, that the phase separation process begins at this time. The signal then increases in intensity for about 30 minutes, and reaches a stable value when the sample is fully cured. At this stage, most of the liquid crystal has phase separated, forming micron sized droplets as shown by scanning electron microscopy.[3]

If no external field is applied to the cured sample, the average direction of the nematic director varies randomly from droplet to droplet. However, when a sufficiently strong external field is applied, the director aligns parallel to the field essentially everywhere. In this case, a normally incident laser beam "sees" the ordinary refractive index n_o of the liquid crystal, and, since the refractive index n_p

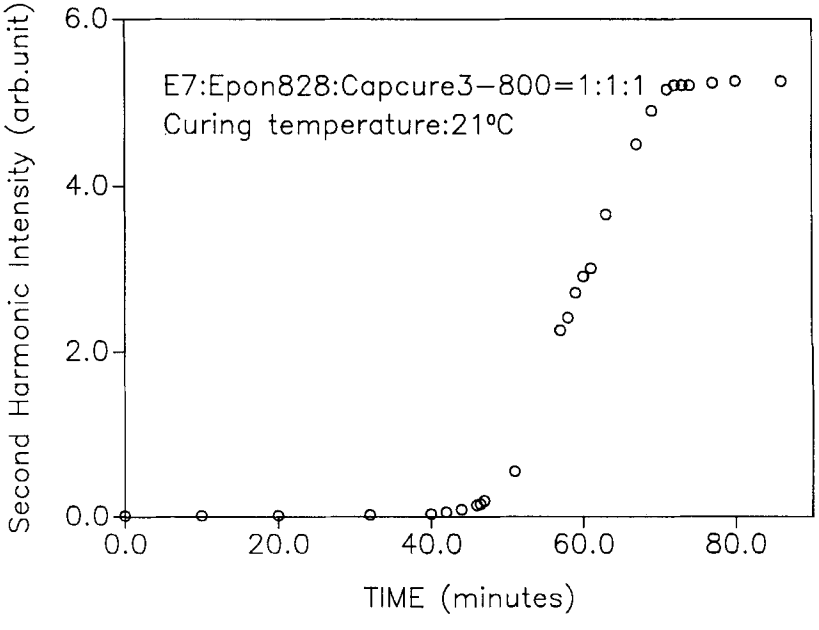

FIGURE 2 Time dependence of the intensity of the SH signal from a 30 μm liquid crystal-polymer mixture. The homogeneous mixture was prepared at t = -540 minutes.

of the polymer is the same as n_o, the film becomes optically clear. The reduction of the dielectric constant difference across the interface for polarization perpendicular to the nematic alignment direction, which occurs at dc as well as at optical frequencies, is expected to reduce the SH intensity. This has been verified by our experiment. Figure 3 shows the SHG intensity from a 10 μm thick PDLC sample as function of applied ac-voltage (f = 60 Hz). Results are shown for measurements at 21°C, where the liquid crystal is in the nematic phase, and at 70°C, where the liquid crystal is isotropic. Figure 4 shows the transmittance of the PDLC film at 532 nm as a function of voltage; comparison of Figures 3 and 4 indicates that the SH intensity starts to decrease at the same threshold voltage where the transmittance starts to increase. This suggests that the bulk orientation of the liquid crystal inside the droplets significantly affects SHG by the film.

Finally, preliminary measurements of the angular distribution of the SHG intensity from a fully cured sample was carried out both with and without an applied a.c. voltage. The normalized result for $I_s(q)$ is shown in Figure 5, while the intensity of linearly scattered light at 1.06 μm is shown in Figure 6. Although application of a voltage across the cell changes the amplitude of the scattered intensity, features such as location of peaks in the scattered intensity are not significantly altered. This suggests that similar to linearly scattered light, the angular dependence of the scattered second harmonic intensity contains information about the structure of the material.

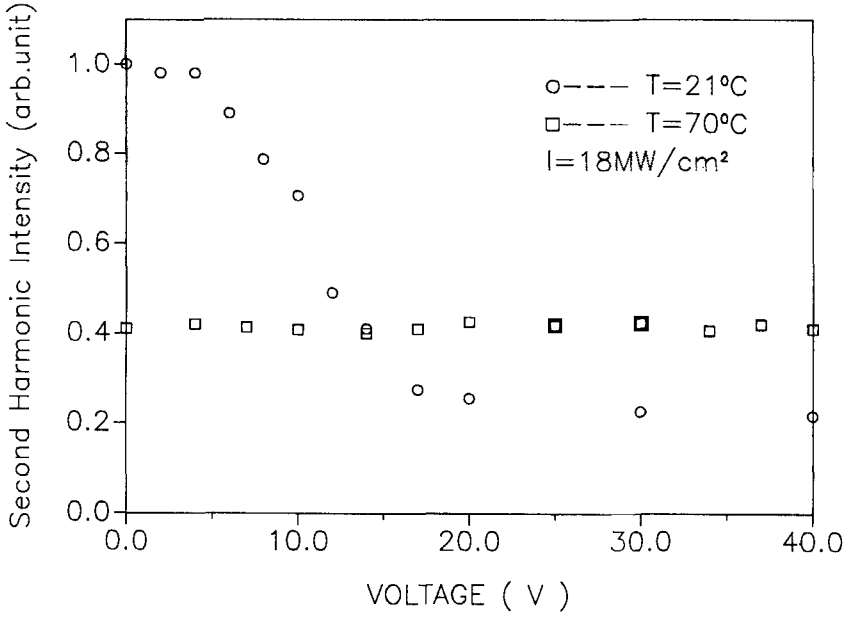

FIGURE 3 Voltage dependence of the intensity of the SH signal from a fully cured 10 μm thick PCLD sample. At 21° the liquid crystal is in the nematic phase, while at 70° it is isotropic.

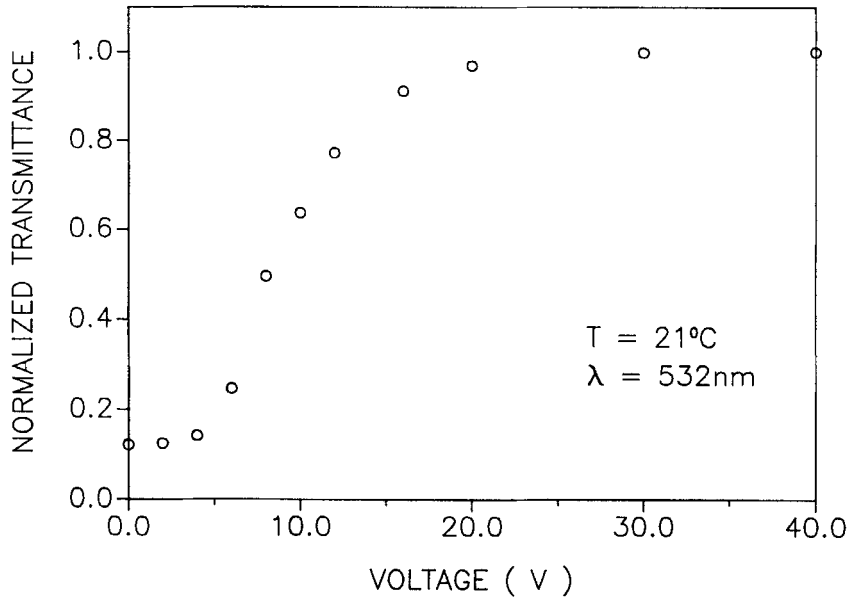

FIGURE 4 The transmittance of the 10 μm PDLC sample at λ = 532 nm as function of rms voltage applied across the cell. f = 60 Hz.

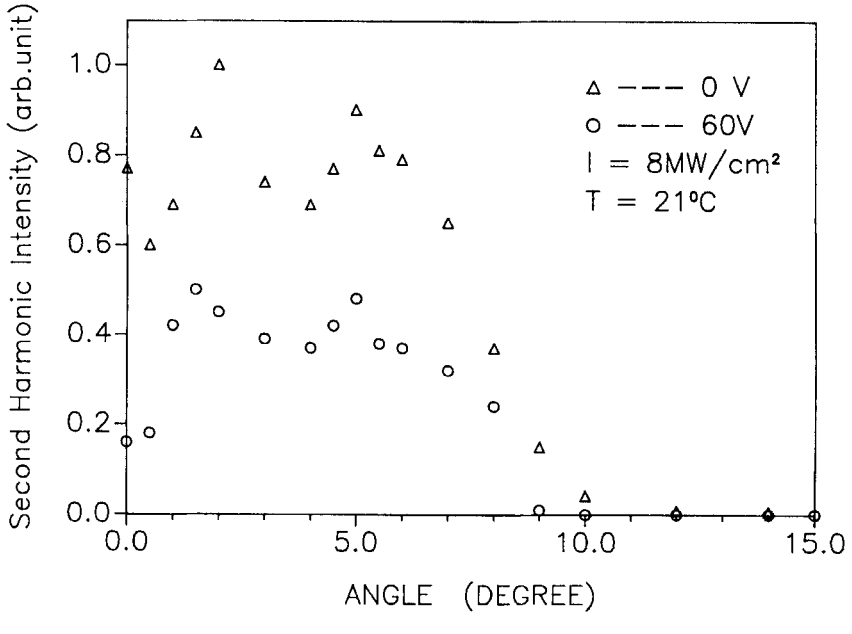

FIGURE 5 Angular dependence of the intensity of the SH signal from the 10 μm PDLC sample.

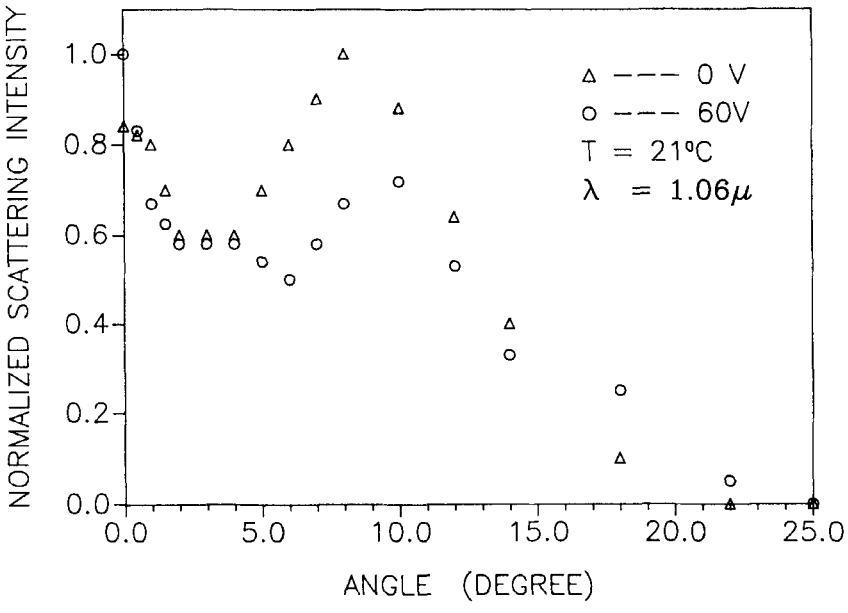

FIGURE 6 Angular dependence of the intensity of linearly scattered light from the 10 μm PDLC sample. λ = 1.06 μm.

DISCUSSION AND CONCLUSIONS

We have observed a second harmonic generation from interfaces in fully cured PDLC samples, and also from concentration gradients during the initial stages of phase separation. In view of this latter observation, we propose that the breaking of inversion symmetry by the gradient of the dielectric permittivity contributes to second harmonic generation in PDLC films and possibly in other inhomogeneous materials. A simple mechanism is suggested below.

A point charge q, placed in an inhomogeneous medium whose dielectric constant varies linearly with position, induces an electric field in space which is nonzero at the point where the charge is located. At this point, to lowest order, the induced field is given, in SI units, by

$$E_{\text{ind}} \simeq \frac{q\nabla\varepsilon}{6\pi\varepsilon^2 r_c} \tag{1}$$

where ε is the dielectric permittivity and r_c is a cutoff length. This field exerts a force $F = qE$ on the charge, destroying inversion symmetry and giving rise to SHG. Results for the case when ε is not isotropic will be given elsewhere. Formally, therefore, dielectric constant gradient induced second harmonic generation would be a third order process, similar to the usual d.c. electric field induced second harmonic generation (EFISH), with the second harmonic polarization given by

$$P(2\omega) = \chi^{(3)}E_{\text{ind}}(0)E(\omega)E(\omega) \simeq \frac{q}{6\pi\varepsilon^2 r_c}\chi^{(3)}\nabla\varepsilon(0)E(\omega)E(\omega). \tag{2}$$

The intensity of the second harmonic signal can be calculated from Equation (2) if $\varepsilon(r)$ is known. Information about $\varepsilon(r)$ can be obtained from conventional light scattering data[4]; however, we have not yet compared our measured SH intensities with the predictions of this model. A crude estimate of the contribution of this mechanism to the surface second harmonic susceptibility $\chi_s^{(2)}$ of an interfacial layer of thickness d can be obtained by noting that

$$\chi_s^{(2)} = \chi^{(3)} E_{\text{ind}} d \simeq \chi^{(3)} \frac{q\Delta\varepsilon}{6\pi\varepsilon^2 r_c} \tag{3}$$

where $\Delta\varepsilon = d\nabla\varepsilon$ is the change in the dielectric permittivity across the layer. Using the electronic charge for q and assuming that $\Delta\varepsilon \simeq 6\varepsilon_0$, $\varepsilon \simeq \varepsilon_0$, $r_c \simeq 5$ Å, that is, that the cutoff length is of the order of a molecular length, and noting that for our liquid crystals the average third order susceptibility determined by EFISH measurement[5] is $\chi^{(3)}(-2\omega;0,\omega,\omega) \simeq 2 \times 10^{-20}$ (SI). We obtain $\chi_s^{(2)} \simeq 4 \times 10^{-21}$ (SI) or 10^{-15} (esu) which is comparable to typically measured values.[3,6] The third order susceptibility of our liquid crystals, measured on the nanosecond timescale, is large (approximately two orders of magnitude greater than CS_2) which may explain the relatively large observed SH intensities.

The proposed mechanism at least qualitatively explains our observations. The onset of SHG corresponds to the onset of phase separation, when concentration and hence dielectric constant gradients appear. As the gradients increase with time to form the interfaces separating the polymer and the liquid crystal, the SH intensity increases as suggested by Equation (2). In the fully cured sample, as the liquid crystal is oriented in the inclusions by an external dc field, the dielectric constant mismatch is decreased, decreasing $\Delta\varepsilon$ across the interface and decreasing the SH intensity. Finally, we suggest that dielectric constant gradient may also play a role in second harmonic generation by nematic liquid crystals where the director field is not uniform.[7]

The angular dependence of the SH signal provides information about the spatial dependence of the dielectric constant gradients. In analogy to conventional light scattering, we expect the second harmonic intensity $I_s(q, t)$ in momentum space to have the form

$$I_s(q) \propto E^4 \int (\nabla\varepsilon(0) \cdot \hat{E})(\nabla\varepsilon(r) \cdot \hat{E}) \exp(iq \cdot r)\, d^3r \tag{4}$$

where $E = E\hat{E}$ is the incident optical field. The measurement of the time evolution of $I_s(q)$ therefore provides information about the structure factor and the kinetics of phase separation. Since only the gradients of ε appear in Equation (4), $I_s(q)$ more sensitively probes the short wavelength dielectric constant variations than conventional linear light scattering. For a given small scattering vector q, the scattering angle for the second harmonic signal is one-half of that for linear scattering if the angles are small. We assume that the peak in the linearly scattered intensity at ~9° in Figure 6 corresponds to the peak at ~5° in the SH intensity in Figure 5. The origin of the peak at ~2° in this figure is not well understood. We note that the signal falls to zero at ~25° in the linear case, and at ~12° for the SH.

From Equation 4 we expect that $I_s(q) = q^2 I(q)$, where $I(q)$ is the linearly scattered intensity. In Figure 5 we also observe a corresponding the decrease of the signal at small q. The large aperture used in these preliminary measurements accounts for $I_s(0) \neq 0$.

In conclusion, we have observed second harmonic generation from PDLC films both during phase separation and in the fully cured state. Our results suggest that the breaking of inversion symmetry by dielectric constant gradients due to variations in composition plays an important role in SHG in these, and possibly other systems. We have proposed a simple physical model of this mechanism, on the basis of which the SH intensity can be calculated. Our preliminary experimental observations are in qualitative agreement with the predictions of this model. A great deal of further theoretical and experimental work is necessary to assess the validity of this approach.

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