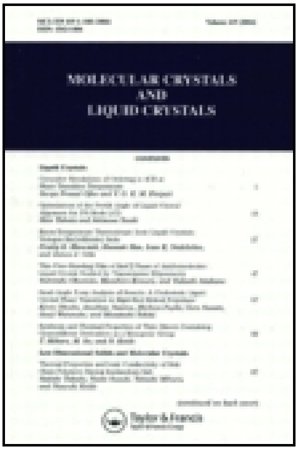

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Investigations of Filled Nematics by Second Harmonic Generation

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INVESTIGATIONS OF FILLED NEMATICS BY SECOND HARMONIC GENERATION

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Abstract We report first measurements of optical second harmonic generation in filled nematics. They were performed in order to clarify open questions about the anchoring conditions in this material, which consists of low portions of pyrogenic silica dispersed in a nematic liquid crystal. We compare the SHG behaviour with that of Polymer Dispersed Liquid Crystals and show that in FN two contributions to SHG with different origins have to be considered.

INTRODUCTION

Filled Nematics (FN) have been demonstrated as a new material for bistable scattering displays [1,2]. They consist of a low portion of highly dispersed pyrogenic silica (Aerosil™ from Degussa), typically 2-3 volume percent, in a nematic liquid crystal (NLC). Chainlike aggregates of primary particles (spheres of about 10^4 SiO_2 units, typical size 16 nm) form larger agglomerates via hydrogen bonding (Figure 1a). When mixing this with a NLC the agglomerates form a three dimensional open network and thus divide the NLC into domains of typical dimension in the range of 100-300 nm (Figure 1b).

FN displays show bistability between a strongly scattering and a transparent state [3]. In the scattering state the orientation of the different nematic domains is randomly distributed. Transparency can be achieved by applying electric fields (Figure 2a) by which the liquid crystal molecules are reoriented. The scattering state is obtained due to laser induced effects or ultrasound (Figure 2b) which destroy the parallel alignment of the LC domains. Both configurations are stabilized by the Aerosil network.

The silica network has virtually no influence on the linear optical properties of the FN display. In the transparent state no dependence on the viewing angle has been observed [1] although the refractive index of the Aerosil is $n_A = 1.45$ and the ordinary refractive index of the NLC is $n_o = 1.52$. This is due to the high volume ratio of the NLC and the smallness of the Aerosil particles only resulting in a very weak Rayleigh scattering which is negligible

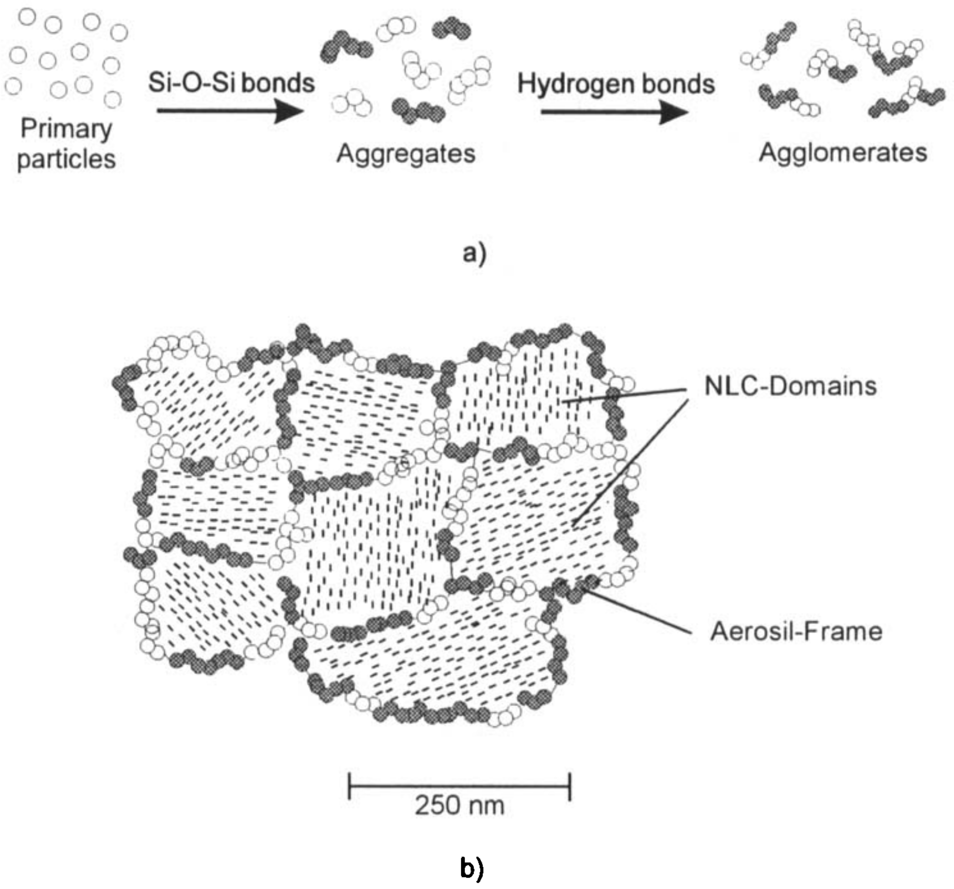


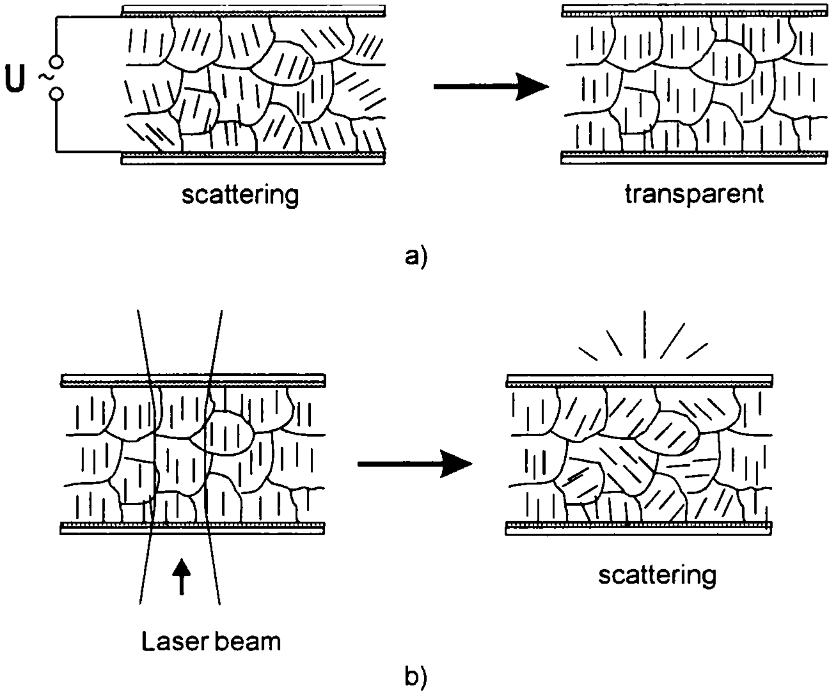
FIGURE 1 Filled nematics (FN): a) Primary particles of SiO_2 are forming aggregates via Si-O-Si bonds. These form larger agglomerates via hydrogen bonds. b) When dispersed in a nematic liquid crystal, Aerosil™ forms a three dimensional open network and thus divides the liquid crystal in domains of typical size about 100-300nm.

compared to the scattering due to LC domains with different orientation.

Up to now there is no satisfactory model for the interaction between the NLC molecules and the Aerosil surface and it is still an open question what kind of anchoring conditions take place in the network. There are only some experimental hints that strong anchoring between the Aerosil and the liquid crystal molecules can be assumed [2].

In principle, two possibilities can be considered. First one can assume that the anchoring between Aerosil and LC is weak and not dominant for the orientation of a single domain. The anchoring then only stabilizes a given orientation and after any reorientation new bonds between LC and Aerosil are formed. This means that the Aerosil network itself is treated as a stable frame in which the LC molecules can be oriented separately.

The second possibility are strong anchoring conditions. This would mean that the Aerosil network determines the orientation of the liquid crystal inside a domain. Orienting



a)

b)

FIGURE 2 Working principle of FN displays: If the directors of the domains are distributed randomly the display is strongly scattering. By applying a voltage the LC molecules are reoriented in the electrical field and the cell becomes transparent (a). Due to laser induced thermal effects, the display can be switched back to the scattering state (b).

the LC molecules must then be accompanied by a change in the network structure itself.

In order to start to investigate the questions mentioned above we can use nonlinear optical phenomena because we expect a high influence of the dispersed material on the nonlinear optical properties of FN. The high specific surface of the Aerosil agglomerates should be an excellent source for surface induced second harmonic generation (Aerosil-LC contribution). But we expect the generation of a second harmonic signal also by dielectric constants differences $\Delta\varepsilon$ in the defect structures of differently oriented liquid crystal domains (LC-LC contribution).

Optical second harmonic generation (SHG) occurs only in noncentrosymmetric materials[4] when we use the electric dipole approximation. There the second order susceptibility tensor $\chi^{(2)}$ is nonzero. In the presence of an electromagnetic field $E(\omega)$ at frequency ω, $\chi^{(2)}$ gives rise to a nonlinear polarisation

$$P_i^{(2)}(2\omega) = \chi_{ijk}^{(2)}(2\omega;\omega,\omega)E_j(\omega)E_k(\omega) \tag{1}$$

which acts as a source in Maxwells equations, resulting in the emission of an electromagnetic field at double frequency 2ω.

Because of their symmetry, bulk liquid crystals or isotropic polymers usually show

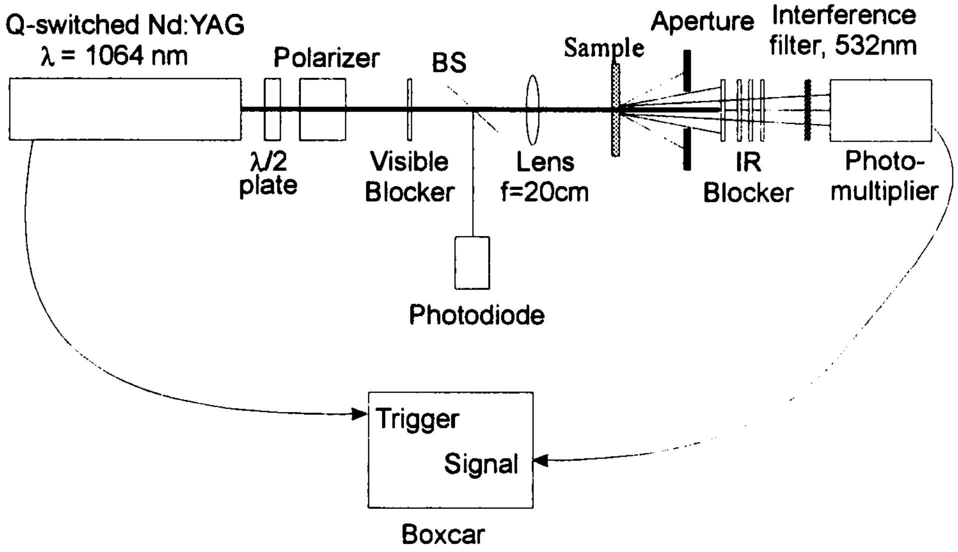


FIGURE 3 The experimental setup.

no SHG, i.e all components of the tensor $\chi^{(2)}$ are zero, except weak contributions due to quadrupole moments [5] which are neglected in the electric dipole approximation. But there are two possibilities leading to SHG in this case also. One is the so called d.c. field induced SHG where an additional static electric field destroys the inversion symmetry and thus gives rise to SHG. The other possibility are surfaces and interfaces between different materials, where there is obviously a lack of symmetry and thus SHG is possible. And indeed this has been demonstrated as a highly surface and interface specific method [6]. It can be used for detecting less than a monolayer of adsorbed molecules on a surface, probing of fast surface dynamics and reactions or mapping the arrangement and composition of surface monolayers.

To point out that it is an effect of the surface/interface we rewrite the susceptibility in Equation (1) as $\chi_s^{(2)}$. The two origins of the surface susceptibility $\chi_s^{(2)}$ are field or structural discontinuities across the surface/interface but only in some special experimental conditions one can distinguish between them.[7,8]

In the following we make the assumption that at an interface between two materials with dielectric constants ε_1 and ε_2 the surface susceptibility is proportional to the mismatch in the dielectric constants, $\chi_s^{(2)} \sim \Delta\varepsilon$. Because the second harmonic intensity is proportional to $|P_s^{(2)}(2\omega)|^2$, we thus have

$$I_{2\omega} \propto \left|\chi_s^{(2)}\right|^2 \propto (\Delta\varepsilon)^2 \tag{2}$$

As we will see, in our case we can vary $\Delta\varepsilon$ and we expect SHG to be an ideal experimental tool to investigate optical composite materials like filled nematics.

As a reference material we used another well known composite material, the so called polymer dispersed liquid crstals (PDLC), whose SHG behaviour has been reported earlier [9].

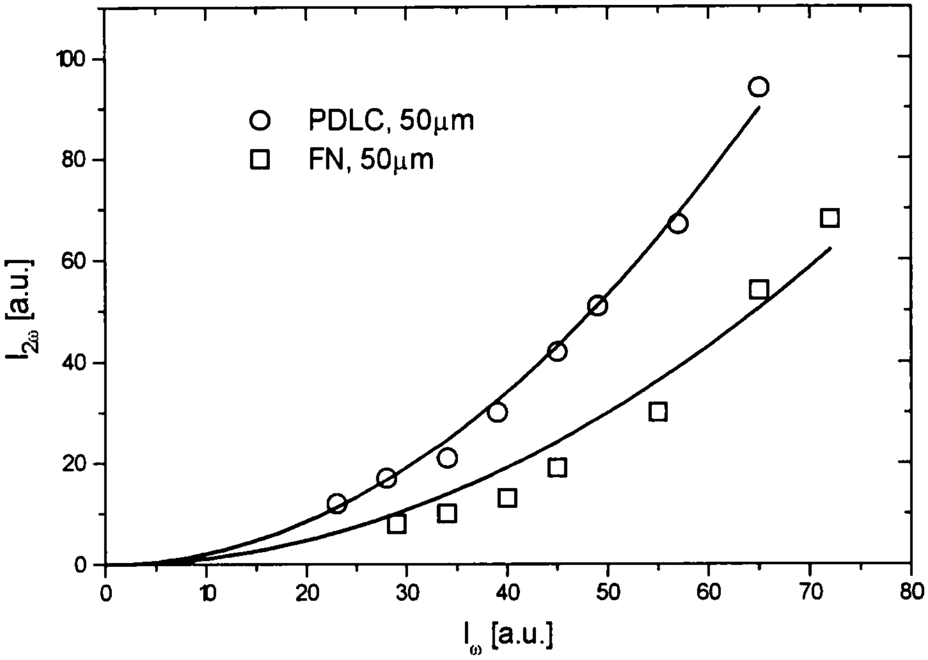


FIGURE 4 Second harmonic intensity $I_{2\omega}$ as a function of the fundamental intensity I_ω for FN (squares) and PDLC (circles) samples. The solid lines are quadratic fits.

PDLC are nematic droplets inside a polymer binder. They are formed by phase separation of an initially homogenous mixture of a polymer and a NLC [10]. In the undriven state, i.e. with no applied voltage, the orientation of the nematic droplets has a random distribution which leads to a strongly scattering state. When a sufficient voltage is applied, the LC molecules are reoriented in the field perpendicular with respect to the cell walls. If the refractive index of the polymer n_p matches the ordinary refractive index n_o of the liquid crystal, a highly transparent state is achieved.

EXPERIMENTS

For the SHG measurements we used a standard SHG setup (Figure 3). The beam of a Q-switched Nd:YAG laser (λ=1064nm) with repetition rates between 2 and 20Hz was slightly focused onto a sample at normal incidence. With the combination of a λ/2-plate and a Glan-prism we could vary the energy of the 10ns pulses. We chose pulse energies around 30mJ giving energy densities around 100mJ/cm^2. At this level, no damage of the samples and no significant thermal effects were observed.

After proper separation of the fundamental signal at 1064nm with the aid of several infrared blocking filters the transmitted light at 532nm was detected by a photomultiplier behind an aperture. The photomultiplier signal was then sent to a boxcar averager and a computer.

In a first experiment, we compared the SHG behaviour of PDLC and FN. The

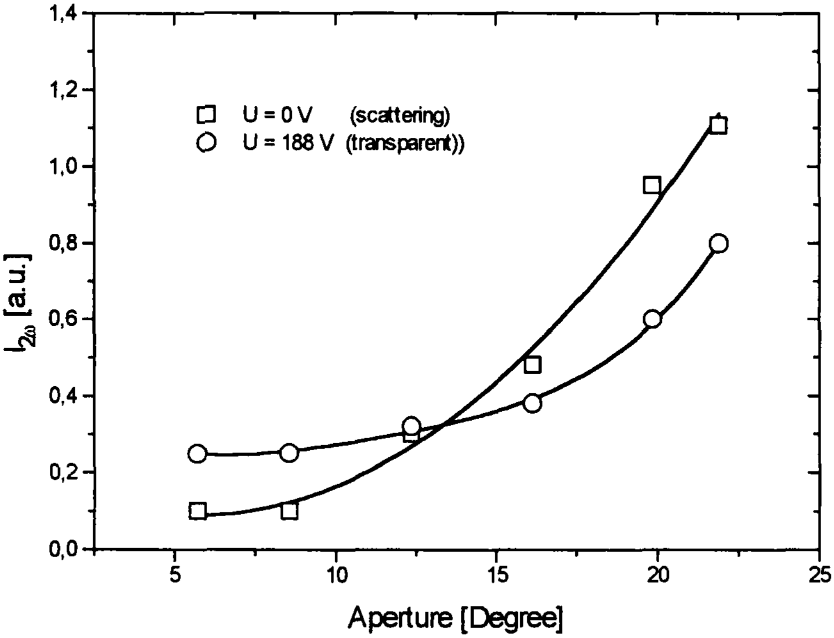


FIGURE 5 SHG signal for a 14µm FN as a function of the detector aperture.

thickness of the scattering samples was 50µm. The PDLC reference sample was produced by mixing the liquid crystal E7 with the prepolymer Epon 828 and the curing agent Capcure 3800. The mixing ratio of the components was 4-3-3. It was thermally cured giving droplets below 1µm in diameter. The ordinary refractive index of the NLC (n_o=1.52) is matched to the polymer (n_p=1.50) whereas the extraordinary refractive index (n_e=1.74) is much larger. In Figure 4 one can see that the measured second harmonic intensities $I_{2\omega}$ were of the same order of magnitude for the both materials and they showed the expected quadratic dependence on the fundamental input intensity I_ω.

It is important to note here that the measured amount of second harmonic light strongly depends on the detection geometry. When we measured $I_{2\omega}$ for a 14µm FN sample while increasing the aperture in the experimental setup and thus the solid angle of detection we observed an increase in the signal (Figure 5, squares). Really surprising was the fact, that even in the transparent state the SHG signal increases with the aperture (Figure 5, circles). Moreover, for small apertures the signal for the transparent sample was larger than that of the same sample in the scattering state.

We interpret this behaviour as follows. First we assume the SHG to be a diffuse process, i.e. the influence of the scattering on the SH intensity is small, an assumption also made by Yuan *et al.* for SHG in PDLC[11]. Second, we have a strong contribution to SHG also in the transparent state. Whether or not this contribution is different in its origin from that in the scattering state has to be discussed in the following. In any case, this shows that the connection between the scattering and the SHG behaviour in FN is more complex, since in PDLC such a behaviour cannot be observed.

When we applied a low frequency voltage to the PDLC sample we observed a decrease in $I_{2\omega}$, while the linear transmittance of the sample increases (Figure 6). This shows that the *only* source for SHG in PDLC is the discontinuity in the electric field due to the gradient in the dielectric properties along the interface between the liquid crystal and the polymer, which vanishes if the refractive index of the polymer (n_p=1.50) is matched to the ordinary refractive index of the liquid crystal (n_0=1.52). This behaviour has been published first by Li *et al* [9]. They demonstrated another proof of this assumption, where they showed that in an originally homogenous mixture of liquid crystal and polymer there is no SHG. But $I_{2\omega}$ increases when the phase separation sets in and liquid crystal droplets are formed inside the polymer matrix.

When we performed the same experiment with a FN sample we observed a qualitatively different behaviour. When applying a voltage we measured an increase for both the linear transmittance and the second harmonic intensity $I_{2\omega}$ (Figure 7). Because in the transparent state all the liquid crystal domains are oriented parallel, the LC-LC contribution to SHG must vanish. The remaining second harmonic signal must be due to the Aerosil-LC interface, because careful experimental investigations have shown that contributions from other sources can be excluded.

Assuming the SHG signal proportional to $(\Delta\varepsilon)^2$ in PDLC the SHG is directly correlated to the strong linear scattering behaviour, while in FN the Aerosil-LC interface gives only a very weak linear scattering as mentioned above. Therefore we try to estimate the different voltage dependences of SHG by a simple model. We take into account the scattering of the incoming fundamental intensity I_ω by

$$\frac{dI_\omega}{dz} = -\sigma_\omega I_\omega \quad , \tag{3}$$

where z is the propagation direction of the laser beam and σ_ω is the attenuation coefficient for scattering. In absence of any phase matching we set for the SHG intensity

$$\frac{dI_{2\omega}}{dz} = \eta I_\omega^2 \quad , \tag{4}$$

i.e. the generation is proportional to $(I_\omega)^2$ and we assume that only unscattered light will generate second harmonic light. The factor η, which describes the efficiency of the light conversion, must be directly proportional to $|\chi_s^{(2)}|^2$ and hence to $(\Delta\varepsilon)^2$. Because $\Delta\varepsilon$ can be changed by applying a voltage $\chi_s^{(2)}$ and η also depend on the applied voltage. We did not introduce scattering losses for $I_{2\omega}$ since we assume the SHG to be diffuse as discussed above. With the boundary conditions $I_\omega(z=0) = I_0$ and $I_{2\omega}(z=0) = 0$, I_ω is then given by an exponential law

$$I_\omega = I_0\, epx(-\sigma_\omega z) \tag{5}$$

and I_{2w} by

$$I_{2\omega} = \frac{\eta I_0}{2\sigma_\omega}\left[1-\exp(-2\sigma_\omega z)\right] \tag{6}$$

With this result, we can derive some information about η using the experimental values for the attenuation coefficient σ_ω. We can get them directly from the transmittance versus voltage curves for λ=1064nm (Figure 6 and 7) since the transmittance T as a function of the applied voltage U can be written as

$$T(U) = \frac{I_\omega(U)}{I_\omega(0)} = \exp(-\sigma_\omega z) \qquad (7)$$

and hence

$$\sigma_\omega z = -\ln(T(U)) . \qquad (8)$$

So σ_ω is not available itself, but for a fixed experimental setup with fixed distance between the sample and the detector, z can be treated as an additional constant factor which does not affect the qualitative behaviour.

As derived by Zumer[12] the scattering for nematic droplets of size R - under the condition $kR>1$ and $2kR(n_1 / n_2 - 1) << 1$, where $k = 2\pi/\lambda$ is the wavenumber and n_1 and n_2 are the refractive indices of the media forming the interface - is proportional to $(\Delta n)^2$ and thus in first order to $(\Delta\varepsilon)^2$. With this information, we can set η proportional to the scattering σ_ω and thus to the experimental values $\sigma_\omega z$ in Equation (8). To take into account SHG contributions which are not affected by an applied voltage we add a second term η_0. With the different experimental curves for PDLC and FN we can evaluate η and η_0. So we use

$$\eta = \eta_1(U) + \eta_0 = -\ln(T(U)) + \eta_0 \qquad (9)$$

to fit Equation (5) to the measurement. The fitted curves are also shown in the Figures 6 and 7 and one can see that they are in a good accordance with the experiments.

For PDLC the best fit was achieved with $\eta_0 \sim 0$. This was expected since for PDLC we knew before that SHG and scattering have the same origin, namely the interface between LC droplets and the surrounding polymer matrix, where the mismatch in the dielectric constants can be made very small so that the SHG signal significantly decreases.

To reproduce the experimental curve for FN we found that η_0 is voltage independent and of the same order of magnitude as η_1 (U=0V). Because the latter corresponds to the LC-LC contribution due to differently oriented LC domains, the first one can be identified as the Aerosil-LC contribution. The voltage independence of η_0 strengthens the assumption of strong anchoring conditions. It shows that the mismatch in the dielectric constants between Aerosil and the liquid crystal is not changed when a voltage is applied.

CONCLUSION

We have measured optical second harmonic generation in filled nematics. We compare the behaviour to that of PDLC and see that the size of the SH signals is of the same order of magnitude for both materials. In contrast to PDLC we have two contributions to SHG in FN with different origins. One arises from different oriented LC-LC domains and behaves in principle like the corresponding only contribution in PDLC, which is the surface between the LC droplets and the surrounding polymer. The other contribution in FN is due to the interface between the Aerosil and the liquid crystal. With a first model, we are able to evaluate the contributions from the experimental data. The Aerosil-LC contribution is

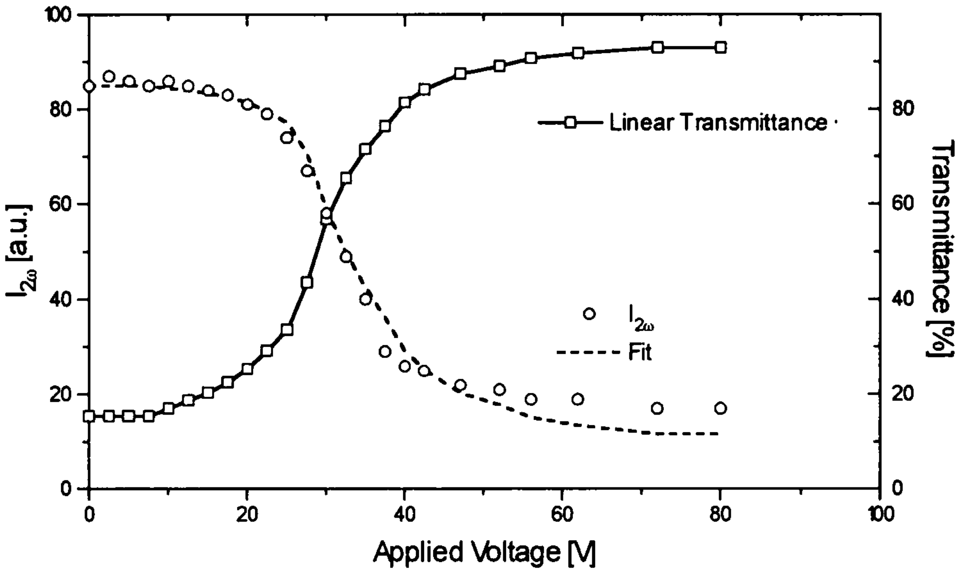


FIGURE 6 Second harmonic signal of a 50μm PDLC sample as a function of applied voltage (circles) and the corresponding transmittance at 1064nm (squares). The dashed line shows the best fit after the model described in the text.

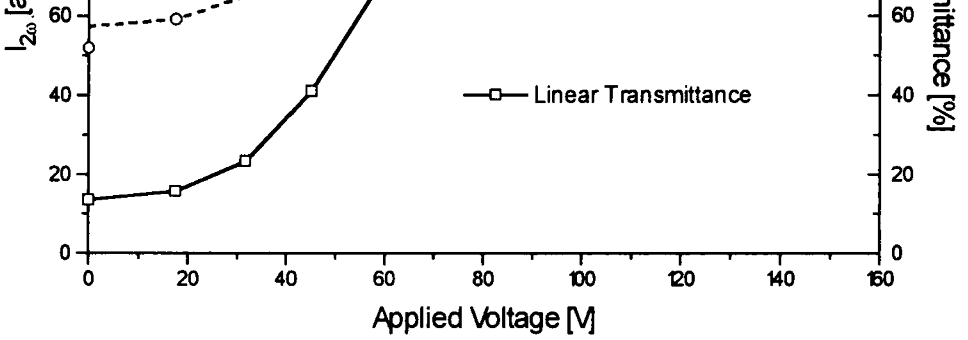


FIGURE 7 Second harmonic signal of a 50μm FN sample as a function of applied voltage (circles) and the corresponding transmittance (squares). The dashed line is the best fit after the model described in the text.

found to be constant and unaffected by the linear scattering behaviour of the FN samples. Therefore the observed second harmonic generation in filled nematics proved to be a good surface-sensitive measuring technique to answer open questions about Aerosil-dispersed liquid crystal systems. With a proper combination of different laser polarization and detection geometries, more information about the anchoring conditions between the Aerosil network and the liquid crystal and eventually of the switching dynamics should be available in the future.

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