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Optical Materials 22 (2003) 289–294



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# Electric field induced second harmonic generation in vacuum evaporated Disperse Red 1 films

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Received 3 May 2002; received in revised form 21 August 2002; accepted 5 September 2002

## Abstract

We have observed the electric field induced second harmonic (EFISH) generation effect on vacuum deposited Disperse Red 1 (DR1) films using corona poling. There is no second harmonic generation (SHG) signal in the absence of the corona. Room temperature corona charging results in an SHG signal which appears and disappears almost instantaneously upon turning on and turning off the corona field respectively. Combined with earlier spectroscopic studies on molecular organization in vacuum deposited DR1 thin film which suggested vertical orientation of most of the molecules, these results clearly indicate that the DR1 molecules in the film are most likely aligned in antiparallel arrangement. The EFISH effect as well as its fast responses to the on–off operation of corona field and the reduction of the SHG signal at elevated film temperature are explained in terms of effective dc field induced polarization effect on the molecules due to third-order nonlinearity of DR1.

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PACS: 42.70.J; 81.15

## 1. Introduction

Photoresponsive organic molecules based on azobenzene (such as those known by the names DO3, DMANAB, DR1, T-azodiol, and DR19) have been known as second-order nonlinear optics (NLO) chromophores. These molecules have been widely investigated as NLO dopants in polymer matrices forming either host–guest composite systems or side-chain polymers [1–4] owing to their high molecular first hyperpolarizability,  $\beta$ . This

parameter is responsible among others, for the well-known effect of second harmonic generation (SHG) i.e. the conversion of light of the frequency  $\omega$  to twice the frequency,  $2\omega$  [5,6]. The organic NLO molecules possessing high  $\beta$  values usually consist of electron donor (D) and acceptor (A) situated at two ends of a bridge (conjugated chain) (B). This molecular structure generally possesses a strong permanent dipole moment.

Organic materials with large second-order susceptibilities are interesting for NLO device applications such as frequency doubling of low power laser diodes, optical data recording and electro-optic modulation. For these applications the materials are usually prepared in the form of thin

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films. In order to produce a macroscopic SHG signal, the molecules in such a film must be aligned with the dipole moment arranged in a parallel fashion, at least to some degree. It is well known however, that organic molecules with strong permanent dipole moment tend to form antiparallel configuration in the condensed phase such as solid film which causes the presence of a center of virtual symmetry. This in turn leads to zero value of the second-order susceptibility  $\chi^{(2)}$  in the related solid materials [7]. Thus, organic compounds of second-order polarizability crystallized in centrosymmetric space groups are generally expected to exhibit no SHG signal in spite of the high microscopic optical nonlinearity  $\beta$  [5–7]. Conversely, the dipole ordering of the deposited molecules can be readily examined by its SHG responses to an incoming monochromatic wave [7].

We have recently reported successful preparation of Disperse Red 1 (DR1) film by physical vapour deposition method on different substrates [8]. Those results indicate that the DR1 molecules in the film prepared by this technique are oriented perpendicular to the substrate or film surface. It remains to be clarified however whether a meaningful dipole ordering is attained in the film. In this work, a decisive answer is provided by the result of SHG observation on the deposited DR1 film. Further corona poling experiment is performed on the film, with the SHG responses measured both in the absence and in the presence of the corona field. This experiment is repeated at different film temperatures.

## 2. Experimental

### 2.1. Sample preparation

The DR1 powder was obtained commercially from Sigma in the form of powder. The structure of the molecule is shown in Fig. 1. As seen in this figure, the DR1 molecule consists of [*N*-ethyl-*N*-2-ethylhydroxy]-amino group as the electron donor group (D), and the nitro electron acceptor group (A), located at the opposite ends of the conjugated chain azobenzene bridge (B). This molecule has a  $\beta$  value of  $125 \times 10^{-30}$  esu [5] (from electric field in-

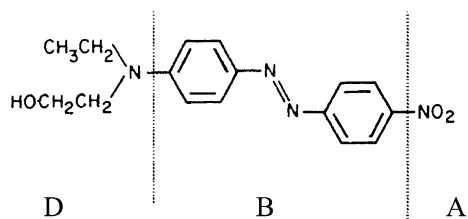


Fig. 1. Molecular structure of DR1.

duced second harmonic (EFISH) measurements at  $\lambda = 1356$  nm).

The DR1 films were deposited on ITO glass substrates in VPC-410 Vacuum Evaporator from Ulvac Sinku Kiko at a pressure of about  $3 \times 10^{-5}$  Torr. The crucible temperature was set at 173 °C, while the substrate temperature was kept at 26 and 55 °C respectively in separate deposition processes.

### 2.2. SHG measurement

The experimental setup for the SHG measurement is sketched in Fig. 2. The SHG signal was measured in situ during the corona poling process. The sample was placed on a temperature controlled metal stage in a horizontal position. A corona needle was positioned at about 6 mm above the sample surface. The positive voltage applied to the corona needle was about 5 kV. A laser beam was made to enter the sample from below at an angle of approximately 45° with respect to the substrate for probing the contribution of dipole moments in both the perpendicular and parallel directions. The beam was derived from a Q-switched Nd:YLF laser operating at 1047 nm as fundamental wave ( $\omega$ ) with the repetition rate of about 400 Hz and pulse width of about 30 ns. The energy per pulse was about 100  $\mu$ J. The beam was weakly focused with a lens of 20 cm focal length. No collecting lens was used for the detector which was a photomultiplier tube (PMT) equipped with filters for blocking the fundamental wave ( $\omega$ ) and passing the second harmonic at 523 nm.

The setup was calibrated with a plate of crystalline quartz positioned in such a way as to produce a signal corresponding to one of the Maker fringes (giving a very strong SHG signal with the laser and PMT parameters used), and with a blank

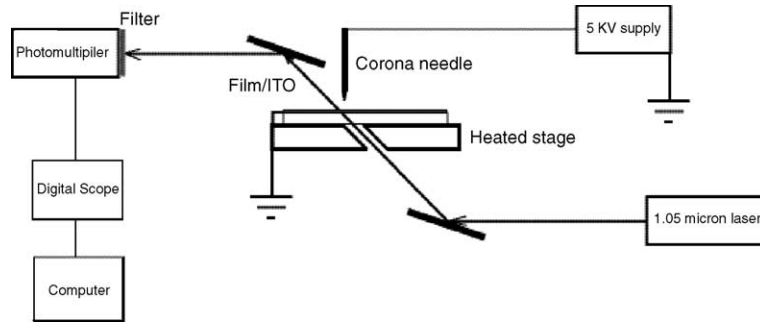


Fig. 2. The experimental setup for the SHG measurement (side view of the poling setup (simplified)). The laser beam enters the stage from below at approximately 45°. The corona needle is located above the stage.

ITO/glass plate which gave no detectable SHG signal with the laser parameters used. The sample positioned on the stage could be corona charged while the SHG signal was being monitored. The SHG signal was observed when the corona was being turned on and turned off. This measurement was first carried out at room temperature on the DR1 film deposited at 55 °C. The measurement was subsequently repeated with temperature of the DR1 film being varied up to 90 °C. The SHG experiments reported here for a nanosecond laser source were further confirmed qualitatively with an additional set of tests using a custom built amplified picosecond laser system delivering 5 ps, mJ range 1064 nm pulses at 20 Hz. Owing to its high fundamental intensities, this system provides exceptionally high sensitivity for the detection of the second-order nonlinearity.

### 3. Results and discussion

The DR1 films obtained from the physical vacuum deposition process were first characterized by DEKTAK IIA depth profiler. The thickness was estimated to be around 0.08 and 0.06  $\mu\text{m}$  for films deposited at 26 °C and 55 °C respectively. The refractive index determined by standard prism coupling measurement was  $n = 1.508 \pm 0.001$  at 632.8 nm.

We found that no sign of SHG signal was observable in this experiment for the as-prepared films. One is thus forced to conclude that, for some reason, there exists a statistical or real centre of

symmetry in the structure of the DR1 film. However, a clear signal was clearly detected when the film was exposed to corona field as shown in Fig. 3. We have found that the SHG signal arising from the film obtained at the higher deposition temperature (55 °C) was stronger than that from the film deposited at lower temperature which is not included in the figure. It is seen from this figure that the film responded almost instantaneously with a clear SHG signal upon application of the corona field, which also decayed almost instantaneously to zero when the corona field was switched off.

Based on our previous results [8] and taking into account the results of SHG measurement described above one may conclude that the molecules of DR1 in the film cannot be vertically oriented

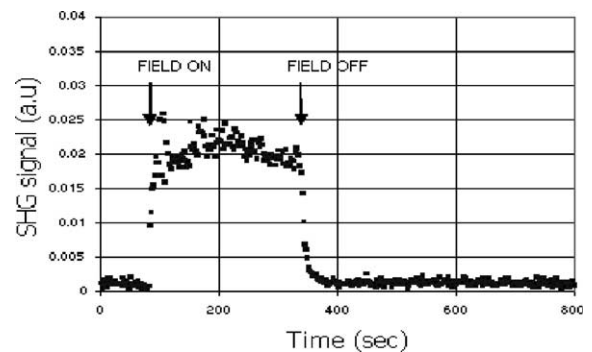


Fig. 3. EFISH response to room temperature poling of DR1 film vacuum evaporated at 55 °C. Note that both the increase of the SHG signal upon turning on the corona and the decay upon turning off the corona are practically instantaneous.

with all-parallel dipole arrangement. Such an arrangement would result in huge SHG signals even in the absence of the poling field, and such signals would be relatively unaffected by the application of poling field in either direction. Indeed, if all DR1 molecules were oriented in a polar fashion perpendicular to the surface, the external field applied perpendicular to the surface would most probably not change the molecular orientation at all. Even allowing some static field induced axial molecular polarization effect, no drastic changes of SHG signal should be observed upon switching on and switching off of the corona field. However, this is in dire contrast to the on–off signal observed in this experiment. The absence of SHG signal without the externally applied electric field and its instantaneous appearance upon application of the field clearly indicate that the original bulk structure is centrosymmetric and only the electric field-induced SHG (EFISH) signal may be observed, similar in some sense to results observed in the guest–host and side-chain electrooptic polymers [3,9–11]. They differ nevertheless in the detailed mechanisms involved as discussed in the following.

The field-induced SHG signal in an amorphous or centrosymmetric systems is known to consist of two components. One component derives from the third-order susceptibility of the material, present in all materials, including those built of centrosymmetric molecules. This EFISH contribution is commonly expressed by the relation:  $\chi^{(2)} \propto \chi^{(3)}E_{dc}$  [5,12,13]. The other component is due to field induced orientation of the dipoles. The possibility of dipole orientation in our DR1 film under the influence of the external field is expected to be very small in view of the molecular ordering and packing reported previously [8]. This leaves us with the other possible contribution (the first component mentioned above) to the observed EFISH signal. For a detailed explanation of this  $\chi^{(2)}$  effect in the special case under study, the film can be regarded as an ensemble of vertically oriented polar molecules with random arrangement in their relative directions (parallel and antiparallel). The application of corona field induces electrostatic polarization or depolarization effect on the individual molecules, depending on the strength of field and the relative direction between

the dipole moment and the external field. This is made possible by the conjugated segment in the DR1 molecule which allows easy displacement of the  $\pi$  electrons along the molecular axis between the electron donor and electron acceptor end groups. It is then natural to expect the induction of preferential polarization effect on the dipole moments; namely slight enhancement for those aligned parallel to the external field and more substantial reduction or even suppression for those aligned opposite to the external field. These effects on the dipole moments is described by the expression  $\mu = \mu_0 + \alpha E + \beta EE + \gamma EEE$ . As a net result, the structure becomes effectively noncentrosymmetric. When the structure is exposed to both a dc field and the optical field at fundamental frequency of  $\omega$ , the component of  $\mu$  at the frequency of  $2\omega$  is also present due to contribution of the last term  $\mu_{2\omega} = \gamma E_0 E_\omega E_\omega$ , which is not being averaged out to zero. This component will, however, disappear as soon as the dc field is removed. The relaxation time depends mostly on the conductivity of the film. This explains readily the on–off behavior of the SHG signal controlled by the corona field, with the near instantaneous responses exhibited by the film limited only by charging–discharging of the film.

Another important observation in this experiment was the decrease of SHG signal from the DR1 film when its temperature was raised during corona poling as depicted in Fig. 4. This is in contrary to the typical behavior of second-order NLO polymers where the thermal agitation facili-

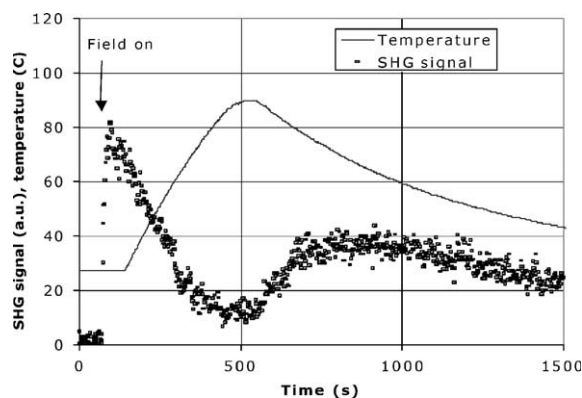


Fig. 4. Thermal effect on SHG signal in DR1 film.

tates the field induced orientation effect leading to enhanced SHG signal [14]. It is interesting to note further that the SHG signal was partially recovered when the film is cooled down under the corona poling, although the recovery process did not persist for some unclear reason. In no case however, any sign of permanent (slowly decaying) SHG was observed. At all temperatures the SHG signal was found to decay to zero quite quickly after turning off the corona field. The effect of temperature on the SHG signal may arise from temperature affected conductivity change or some thermally induced structural changes of the molecules in the film, resulting in less effective changes of the local field effect. It is clear nevertheless that further experiment is required for more detailed understanding of this temperature effect. In a nutshell, unlike in poled polymers where the rise and the decay of the SHG intensity is known to occur through the thermally activated reorientation of the NLO chromophores, the orientations of DR1 dipoles in the film are not changed by the electric field and only static electric polarization mechanism is operative as explained earlier.

To quantify the SHG susceptibility observed in these corona poling experiments, the SHG signal from the film was compared with the signal at one of the Maker fringes of a quartz plate. The experimental values of SHG susceptibility  $\chi^{(2)}$  induced by corona poling in the DR1 film was thus approximately estimated to be 10 times the  $d_{11}$  value of quartz. From the reported value of  $d_{11} = 0.5$  pm/V of quartz [3], the SHG susceptibility  $\chi^{(2)}$  of DR1 during the corona poling was close to 10 pm/V. It is important to point out that this value is more than one order of magnitude smaller than the value reported for electrically poled film of DR1 copolymerized with MMA (168 pm/V) [15] and the maximum value (220 pm/V) obtained in silica film doped with 40 W% of DR1 at Nd:YAG laser wavelength [16]. It is interesting to note, however that the same report showed a sharp drop from this value at higher DR1 content as the aggregation effect began to set in, leading to centrosymmetric dipole ordering. The DR1 molecules in our film are arranged in antiparallel dipole order as concluded in this experiment and subsequently demonstrated by the associated remark-

able aggregation effect [17]. Therefore the associated  $\chi^{(2)}$  value is strongly limited by the smallness of  $\chi^{(3)}$  value as explained earlier. One may further wonder whether this susceptibility is consistent with that expected on the basis of the third-order nonlinearity of DR1 molecules. This is not possible to discuss without the knowledge of the actual poling field present in the film during the corona poling process. However, one should note that the value of  $\chi^{(2)}$  on the order of  $10^{-11}$  m/V can be readily obtained if the field is of the order of  $10^8$  V/m (fields of the order of hundreds volts per micron are typical in poling experiments) and  $\chi^{(3)}$  ( $-2\omega; \omega, \omega, 0$ ) of the order of  $10^{-19}$  m<sup>2</sup>/V<sup>2</sup> is quite a likely value for the DR1 film.

#### 4. Conclusions

Based on the results of SHG measurements we conclude that DR1 molecules which have been previously found to be vertically oriented in a vacuum evaporated film are likely aligned antiparallel to each other, as evidenced by the absence of SHG signal without the presence of external electric field. It is possible, however to induce a SHG susceptibility in DR1 films by corona poling. The EFISH effect characterized by its near instantaneous responses and its reduction at elevated film temperature is explained in terms of field-induced static polarization of the molecules in the film.

#### References

- [1] M.S. Ho, A. Natansohn, P. Rochon, *Macromolecules* 29 (1996) 44.
- [2] Z. Sekkat, D. Morichere, M. Dumont, R.L. Saibi, J.A. Delaire, *Journal of Applied Physics* 71 (3) (1992) 1543.
- [3] N. Tsutsumi, O. Matsumoto, W. Sakai, T. Kiyotsukuri, *Macromolecules* 29 (1996) 592.
- [4] S. Hu, G.O. Carlisle, D.R. Martinez, *Journal of Materials Science Letters* (1992) 794.
- [5] P.N. Prasad, D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley & Sons Inc., New York, 1991.
- [6] K.D. Singer, M.G. Kuzyk, J.E. Shon, *Journal of the Optical Society of America B: Optical Physics* 4 (1987) 968.
- [7] J. Abe, M. Hasegawa, H. Matsushima, Y. Shirai, *Macromolecules* 28 (1995) 2938.

- [8] H. Taunaumang, Herman, M.O. Tjia, *Optical Materials* 18 (2001) 343.
- [9] M.A. Firestone, M.A. Ratner, T.J. Marks, *Macromolecules* 28 (1995) 6296.
- [10] M. Chen, L. Yu, L.R. Dalton, Y. Shi, W.H. Steier, *Nonlinear Optics* 1409 (1991) 202.
- [11] P.A. Chollet, G. Gadret, P. Raimond, F. Kajzar, *Nonlinear Optics* 14 (1995) 47.
- [12] S. Horinouchi, G.J. Zhang, T. Kinoshita, K. Mito, K. Sasaki, *Nonlinear Optics* 14 (1995) 301.
- [13] S.P. Karna, Y. Zhang, M. Samoc, P.N. Prasad, B.A. Reinhardt, A.G. Dillard, *J. Chem. Phys.* 99 (12) 9984.
- [14] S. Schussler, R. Richert, H. Bassler, *Macromolecules* 28 (1995) 2429.
- [15] T. Kaino, S. Tomaru, *Advanced Materials* 5 (3) (1993) 172.
- [16] O. Sugihara, M. Furukubo, H. Hayashi, N. Okamoto, *Nonlinear Optics* 14 (1998) 251.
- [17] H. Taunaumang, R. Hidayat, Herman, M.O. Tjia, in preparation.