ELSEVIER

Dyes and Pigments, Vol. 31, No. 3, pp. 225–232, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/96/$15.00 + 0.00

0143-7208(95)00103-4

Optical Second Harmonic Generation in Corona-poled Polymeric Colorant Films

Xin Zhong,[a]* Huang Deyin,[a] Wang Binkui[b] & Zhai Xianghua[b]

[a]Research Institute of Speciality Chemicals, East China University of Science and Technology,
130 Meilong Road, Shanghai 200237, Republic of China
[b]Department of Physics, ECUST, Shanghai 200237, Republic of China

(Received 20 August 1995; accepted 8 November 1995)

ABSTRACT

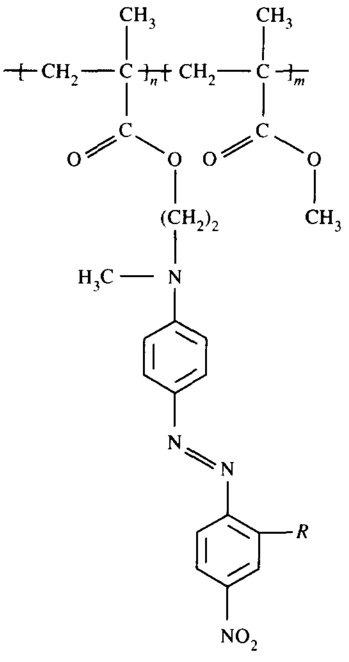
The second harmonic properties of thin films of polymeric colorants covalently linked to azo dyes were determined and the effects of poling time, poling temperature and poling electric fields on the SHG were evaluated. A poling temperature around the T_g *of the polymeric colorants, a poling time between 20~30 min and a poling electric field at 5 kV/cm*^{2} *were found to be suitable conditions. The decay of the second harmonic coefficient of the polymeric colorants and of the dye/PMMA mixed system corona-poled films was compared. It was concluded that films of the polymeric dyes have more potential for use as practical nonlinear optical materials than dye/PMMA mixed systems. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

It is generally recognized that donor–acceptor substituted organic compounds such as benzenes, stilbenes and azo dyes possess large molecular second-order nonlinear optical susceptibilities.[1,2] A number of workers[3,4] have examined the NLO (nonlinear optical) properties of such molecules dispersed in glassy polymer hosts and in liquid crystalline polymer hosts. However, host–guest systems suffer from limited solubility of the NLO molecule in the polymer host, and orientation in glassy polymer matrices is gradually lost over a few days at room temperature.[3]

---

* Corresponding author.



Ia: $R = NO_2$ Ib: $R = CN$

Fig. 1. The structure of polymeric colorant.

A more advantageous arrangement is to connect the active NLO species covalently to the polymer backbone. Herein, we report such polymers with covalently bound azo dyes,[5] as shown in Fig. 1.

The second harmonic generation in transmission through the films, d_{33}, was measured by the Maker Strip method using a YGA laser. The factors influencing the SHG of the poling time, poling temperature and poling electric field were studied. The decay of the second harmonic coefficient of the polymeric colorant and of the dye/PMMA (guest–host) system in corona-poled films was compared. It was found that stable, high orientated and ordered levels of NLO-active material could be achieved.

EXPERIMENTAL

Film preparation and poling

The polymeric colorant (**Ia** or **Ib**) films were prepared by spin-coating. A solution of **Ia** or **Ib** in chlorobenzene was spin-coated at 1500 rpm onto a

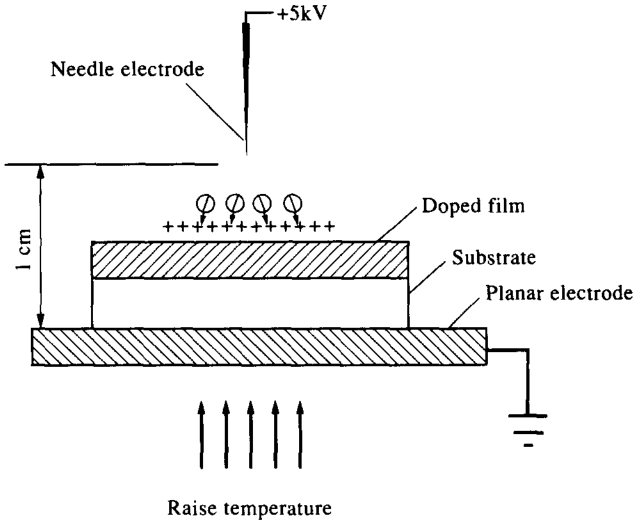


Fig. 2. Needle-electrode poling configuration.

1-mm-thick transparent microscope slide followed by a soft bake at 60°C for 30 min to remove residual solvent. The film thickness was measured with a profilometer, and each sample yielded thickness values in the range of 1 μm.

The films were poled at selected temperatures and times, using a needle-electrode poling configuration, as shown schematically in Fig. 2. The film was then cooled to room temperature with the electric field still applied. Finally, the field was removed, resulting in a system where the nonlinear optic molecules were aligned within the polymer matrix. Since the operating point of the corona-onset discharge did not exhibit the characteristic bluish-white sheath associated with a full positive corona discharge, and since the poling was performed at an elevated temperature, this type of poling is referred to as COPET.

Measurements of SHG signal

In general, the second harmonic power in a uniaxial material is given by eqn (1).[6]

$$P^{2\omega} = (512\pi^2/A)t_\omega^4 T_{2\omega} d^2 p^2 P_\omega^2 \times 1/(n_\omega^2 - n_{2\omega}^2)^2 \sin^2\psi(\theta) \qquad (1)$$

where A is the area of the laser beam spot, P_ω is the incident laser power, t_ω and $T_{2\omega}$ are Fresnel-like transmission factors, n is the refractive index at the indicated frequencies, and ψ (θ) is the angular dependence of the second harmonic power resulting from interference between free and bound waves.

When the coherence length $L_c = \lambda/4(n_\omega - n_{2\omega})$ is large compared with the film thickness, $\sin^2\psi\,(\theta)$ can be expanded for small $\psi\,(\theta)$, leading to eqn (2):

$$\sin^2\psi(\theta) \sim \left[\frac{\pi}{2}\frac{L}{L_c}\frac{\bar{n}}{(N^2 - \sin^2\theta)^{1/2}}\right]^2 \tag{2}$$

where $\bar{n} = (n_\omega + n_{2\omega})/2$ and $N^2 = \bar{n}^2 + [(n_\omega - n_{2\omega})/2]^2$.
Since $(n_\omega - n_{2\omega})\bar{n}$, the second harmonic intensity is independent of the coherence length. The expression d^2p^2 is determined by the form of the nonlinear susceptibility tensor, and the geometry of the experiment. The film preparation technique used in this investigation results in a material possessing a unique axis in the direction parallel to the field direction within the point group ∞mm. There are then five nonzero tensor components, three of which are independent. With the three axis the unique axis, one finds that with d_{31} $(= d_{21})$, d_{33} and d_{24} $(= d_{15})$, Kleinman symmetry gives $d_{15} = d_{31}$, and the method of film preparation gives $d_{31} = d_{33}/3$. The polarization of the second harmonic has the form shown in eqn (3).

$$\begin{aligned} P_x^{2\omega} &= 2d_{15}E_xE_z \\ P_y^{2\omega} &= 2d_{15}E_yE_z \\ P_z^{2\omega} &= d_{31}E_x^2 + d_{33}E_z^2 \end{aligned} \tag{3}$$

where the standard reduced notation has been used, with the incident laser light polarized, and projecting the incident electric field onto the film non-

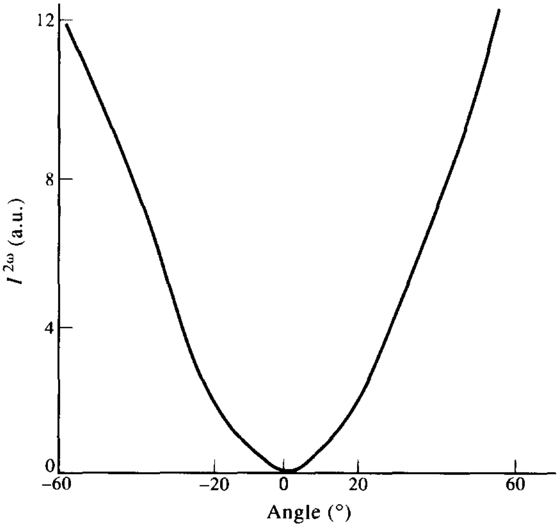


Fig. 3. Second harmonic light vs incident angle for a poled film of **Ia**.

linear polarization components. Under these conditions, $d = d_{33}$ and eqn (4) pertains.

$$P = (\cos^2\theta_\omega/3 + \sin^2\theta_\omega)\sin\theta_{2\omega} + \cos\theta_\omega\sin\theta_\omega\cos\theta_{2\omega} \qquad (4)$$

Using second harmonic generation in transmission through the films, d_{33} was measured. The transmitted second harmonic intensity is a function of the angle (θ) between the incident fundamental beam and the film normal as shown by the typical data in Fig. 3.

The measurements were made on a q-switched Nd: YAG laser with a 1.064-μm wavelength. The value of d_{33} was determined by comparison to d_{11} of quartz measured under the same conditions.

RESULTS AND DISCUSSION

Poling time

After films of the polymeric colorant **Ia** were poled at 5 kV/cm^2, 110°C and different poling times, the d_{33}-value of the films was determined. The results are shown in Fig. 4 and indicate that the longer the poling time, the higher the second harmonic intensity (SHI). Moreover, when the poling time was over 30 min, the SHI approached a constant value. The orientation order of the colorants in the polymer is time dependent. The longer the poling time, the more ordered the colorant molecules become in the polymer, and the SHI values of the films become larger. When the poling time is sufficiently long, all guest molecules in the polymer are poled to a degree which imparts non-linear optic properties to the system and the SHI value approaches a constant value.

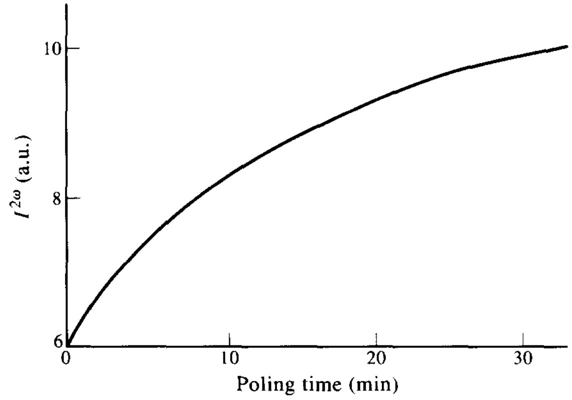


Fig. 4. Relationship between SHG and poling time.

Poling temperature

Ia films were poled at different poling temperatures (5 kV/cm^2, 6~10 μA, 10 min), after which the films were cooled to room temperature and the SHI value was determined. The results are shown in Fig. 5 and indicate that the SHI reaches a maximum value when poling temperature is around the T_g (110°C). This is the reason why on raising the temperature close to the T_g, the film becomes soft and the rotation of the colorant molecules in the polymer occurs readily during poling. On cooling, the guest molecules are frozen into their new orientation, imparting nonlinear optic susceptibilities.

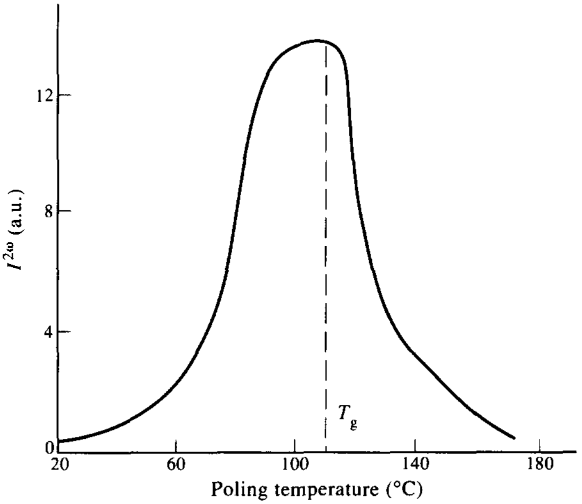


Fig. 5. Relationship between SHI and poling temperature.

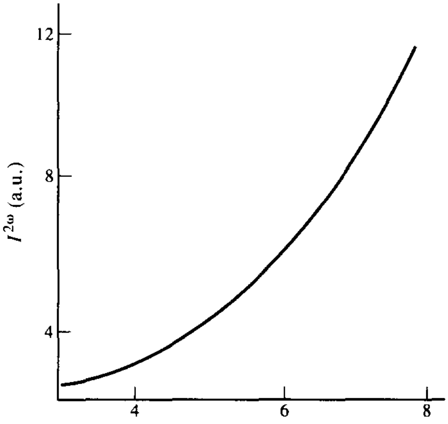


Fig. 6. Relationship between poling electric field and second harmonic intensity.

Poling electric field

Ia films were poled at 110°C for 5 min with the applied electric field being varied from 3 to 8 kV/cm^2. The results are shown in Fig. 6, which indicates that the SHG signal intensity increased with increasing poling electric field. This may be attributed to more molecules aligning for the nonlinear optic activity under the applied stronger electric field. Since the magnitude of the second order nonlinear properties of the guest–host film system is directly proportional to the orientational order of dye molecules and because film was easily damaged under too strong an electric field, in general, the applied poling electric field was about 5 kV/cm^2.

Decay of the second harmonic coefficient of polymeric colorant films and dye/PMMA dopant films

Our approach was to dope the PMMA films with polymeric colorant monomers, viz. 4′-[(2-methacryloxyethyl)methylamino]-2,4-dinitroazobenzene (**IIa**) or 4′-[(2-methacryloxyethyl)methylamino]-2-cyano-4-nitroazobenzene (**IIb**). The dye/PMMA (**IIa**/PMMA or **IIb**/PMMA) dopent films and polymeric dye films were poled under identical conditions. The decay of SHG intensity with time was examined (Fig. 7), and the second harmonic intensity continued to decrease at a slower rate. Moreover, over a longer period of time, the decay constants of polymeric dye films were typically smaller than those of dye/PMMA dopant films. Figure 7 shows that the copolymer (polymeric dye film) alignment decays to ~85% of the original value, while that of the guest–host system (dye/PMMA depant film) decays to ~50%.

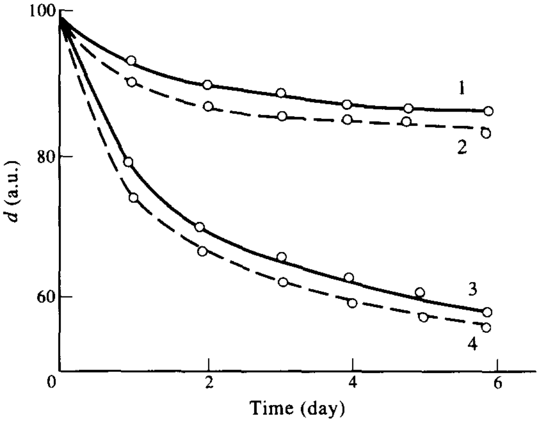


Fig. 7. Decay of second harmonic coefficient of polymeric colorant and dye/PMMA films.

In this case the polymer chains may have begun to relax, and dopant dye molecules that were earlier locked into alignment have greater freedom to rotate and decrease the SHG coefficiency. In addition, one end of the dye molecules in the polymeric dye films is fixed to the polymer backbone and the dye moieties have less freedom to rotate than those in PMMA films doped with the dyes. Thus, the loss in SHG intensity of polymeric dye with time is smaller than for a dye/PMMA mixed system. It is concluded that the films of polymeric dye have more potential use as practical nonlinear optical materials than dye/PMMA mixed systems.

CONCLUSIONS

The magnitude of the second order nonlinear properties of a polymeric colorant film was found to be directly proportional to the orientational order of the colorant molecules, and SHG was influenced by the poling time, the poling temperature and the poling electric field. The most suitable conditions were when the poling temperature was around T_g of the polymeric colorants, the poling time was 20–30 min and the poling electric field was 5 kV/cm^2. The decay of the second harmonic coefficient of the polymeric colorants and of the dye/PMMA doped system films was compared. The second order nonlinear optic coefficients of **Ia** and **Ib** copolymer film decayed to 90% of the original value after 6 days. Films of polymeric colorants are thus more useful as practical nonlinear optical materials than dye/PMMA mixed systems.

ACKNOWLEDGEMENT

This work was supported by the China State Foundation of National Science.

REFERENCES

1. Chemla, D. S. & Zyss, J., *Nonlinear Optical Properties of Organic Molecules and Crystals*. Academic Press, New York, 1987, pp. 51–67, 221–230.
2. Williams, D. J. (ed.), Nonlinear optical of organic and polymeric materials, ACS. *Symposium Series 233, American Chemical Society*, Washington, DC, 1983, pp. 27–35, 81–109.
3. Meredith, G. R., VanDusen, J. G. & Williams, D. J., *Macromolecules*, **15** (1982) 1385.
4. Hompsch, H. L., Yang, J., Wong, G. K. & Torkelson, J. M., *Macromolecules*, **21** (1988) 528.
5. Xin Zhong, Ph.D. thesis, East China University of Science & Technology, 1994.
6. Jerphagnon, J. & Kurtz, K., *J. Appl. Phys.*, **41** (1970) 1667.