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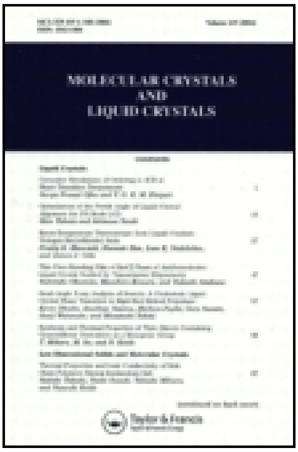

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Observation of Third-Harmonic Generation in Polydiacetylene Films Using Internal Reflection Geometry

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Version of record first published: 24 Sep 2006.

To cite this article: Masashi Kiguchi , Mldori Kato & Yoshio Taniguchi (1995): Observation of Third-Harmonic Generation in Polydiacetylene Films Using Internal Reflection Geometry, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 101-106

To link to this article: http://dx.doi.org/10.1080/10587259508033980

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Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 101–106
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OBSERVATION OF THIRD-HARMONIC GENERATION IN POLYDIACETYLENE FILMS USING INTERNAL REFLECTION GEOMETRY

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Abstract We have demonstrated technique for measuring the third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ based on internal reflection. Using this technique, we observed third-harmonic generation from a poly-DCH film deposited on oriented LB film of poly(3BCMU). Its $\chi^{(3)}$ was 2.1 times as large as an another film with no LB film. This suggests that the oriented LB film contributes to the alignment of the DCH monomer deposited on it.

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INTRODUCTION

Third-order nonlinear optical phenomena can be used for various applications to control light intensity, phase, wavelength, and so on. However, the third-order nonlinearity of general materials is too small to be used for practical applications. Resonance enhancement with real excitation is one possible solution. In this case, its response speed is limited by a lifetime of the excited state, therefore, various contrivances have been demonstrated to decrease the lifetime. Another solution is synthesizing materials that have large nonlinearity. Nonlinear effects with no real excitation respond in femt-seconds, so very fast operating devices are expected using these materials. The third-order nonlinear optical susceptibilities ($\chi^{(3)}$) for a variety of materials have been investigated.

Poly-diacetylene (PDA) has extremely large $\chi^{(3)}$ in off-resonant region.[1,2] Because orienting polymer chains is important for obtaining a large macroscopic nonlinearity, oriented PDA films have been prepared by the vapor deposition and Langmuir-Blodgett (LB) techniques.[3,4]

Several techniques for measuring $\chi^{(3)}$ have been demonstrated; for example, Maker-fringe of the third harmonic generation (THG), four wave mixing and Z-scan. Because THG observation is an easy and highly sensitive method, it has often been used for evaluating new materials. We have developed a new technique based on total reflection for measuring efficiencies of second-harmonic generation (SHG) using powder crystals.[5,6] In this paper, we discuss its application to PDA films for THG. We measured and compared the $\chi^{(3)}$ of poly-diacetylene films deposited on different substrates. Measurements of linear optical dichroism give the degree of polymer chain orientation. However, the absorbance of thick films is too large to observe any transmittance spectra, and scattering owing to their optical roughness distorts reflection spectra. For such films, measurements of $\chi^{(3)}$ with internal reflection geometry were performed to obtain the degree of polymer chain orientation in the films.

EXPERIMENT

The experimental setup is shown in Figure 1. Fundamental waves (λ = 1596 nm) were generated by an optical parametric oscillator (OPO; BMI, OP901) pumped by Q-switched Nd:YAG laser (BMI, 501DNS710). TH power generated in a quartz single crystal was monitored to compensate a fluctuation of the laser power. Both the polarization of fundamental waves and the c-axis of the rutile (TiO_2) prism with hemicylindrical shape are perpendicular to the paper face.

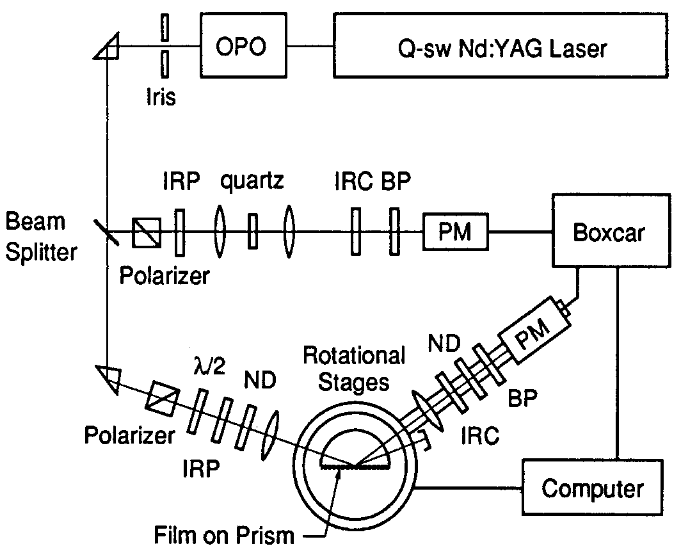

FIGURE 1 Experimental setup. IRP, IRC, ND and BP represent an infra-red pass filter, an infra-red cut filter, a neutral density filter and a bandpass filter, respectively.

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TH waves from the sample were observed in the direction of θ_R defined by

$$n_p^{\omega} \sin\theta_{in} = n_p^{3\omega} \sin\theta_R, \tag{1}$$

where n_p^{ω} and $n_p^{3\omega}$ are refractive indices of the prism at ω and 3ω. The refractive indices were calculated by Selmeir's equation to be 2.71 and 2.98, respectively. The hemicylindrical shaped prism with sample film was rotated to set the incidence angle of the laser beam. The photomultiplier (PM) set on the rail was rotated to adjust the observation angle calculated from Equation (1). Other conditions were same as the conditions for SHG measurement already reported.[6]

A highly oriented monolayer film of poly(3BCMU) was put on the prism by the LB technique.[4] Here, poly(3BCMU) is an abbreviation for poly[4,6-decadiyne-1,10-diol bis([(n-butoxycarbonyl)methyl]urethane)]. The polymer chains were parallel to the c-axis of the prism and the polarization of the fundamental waves. DCH-diacethylene monomers (1,6-bis(N-carbazolyl)-2,4-hexadiyne) were evaporated and deposited on the film. Another film was prepared, that is, DCH monomers were directly deposited on another prism with no LB film. Both films were simultaneously deposited in a chamber. Hereafter, the former is called film A and the latter is called film B. Both of monomer films were thermally polymerized at 150 °C in 24 hours. Each polymerized film was about 2 μm thick , measured with Alpha step 250 (TENCOR INSTRUMENTS). Figure 2 shows the molecular structures of the DCH monomer and the poly(3BCMU).

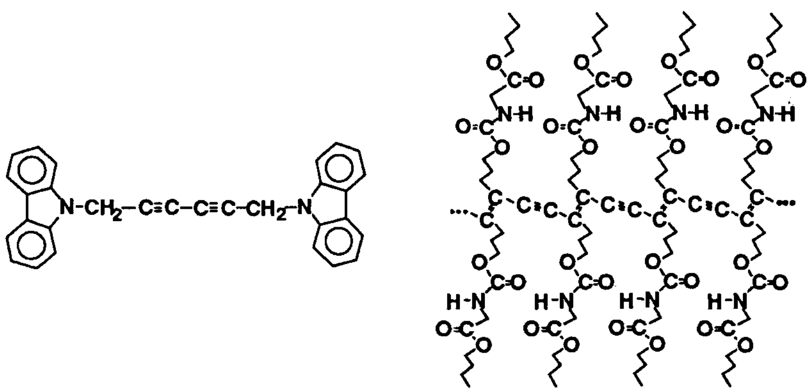

FIGURE 2 Polydiacetylene structures. DCH monomer (left) and poly(3BCMU) (right).

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The deposited films had a few small cracks and optically rough surfaces, which scatters waves. Measurements were carried out at an area in which no cracks were found.

RESULTS AND DISCUSSION

Figure 3 shows the TH power at various incidence angles of the fundamental waves. Open circles and closed circles represent signals from film A and film B, respectively. Curves were the least-squares-fits of equations, which had generally been given by Bloembergen *et al.*, to the experimental values. In our case, complex refractive indices were used, because PDA has a strong absorption at 3ω. The curves fit well with the experimental data, considering the bad quality of the films. Sample refractive indices were also obtained as fitting parameters to be 1.8 for ω and 2.0 for 3ω. Complex refractive index at ω was required to get good fitting, which may be due to the scattering of fundamental waves.

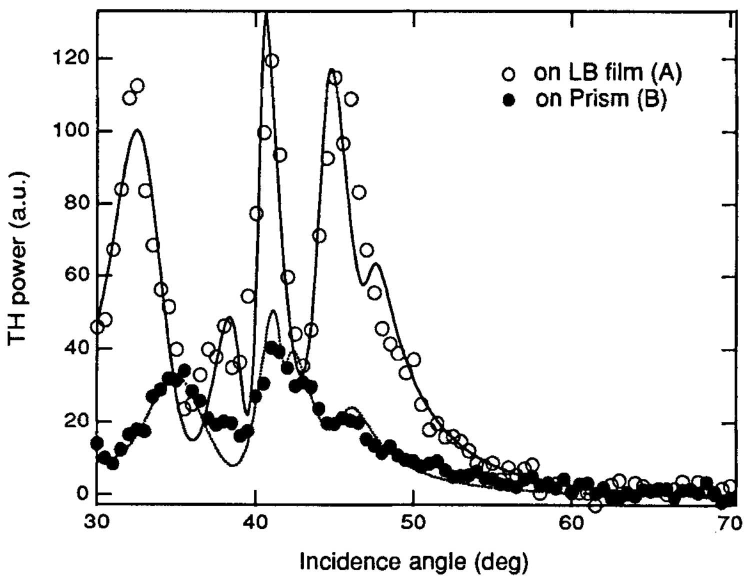

FIGURE 3 TH power at various incidence angles of the fundamental waves measured using internal reflection geometry.

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Each $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the film was provided as one of the fitting parameters. The ratio was

$$\chi_A^{(3)}/\chi_B^{(3)} = 2.1, \tag{2}$$

which means that the vapor deposited film was aligned due to the oriented LB film. Here, we can neglect $\chi^{(3)}$ of the monolayered LB film. Although the degree of orientation in the film might have a depth dependence, the model equations we used do not include this contribution. As $\chi^{(3)}$ consists of the product of four dipole moments, the ratio of $\chi^{(3)}$ for completely oriented one-dimensional nonlinear polarization to $\chi^{(3)}$ for randomly distributed nonlinear polarization is written as

$$1/\left(\langle\cos^4\theta\rangle\langle\cos^4\phi\rangle\right) = 64/9, \tag{3}$$

where θ and ϕ are Eulerian angles. The degree of orientation for film A was small in comparison with Equation (3). The vaporization and deposition conditions for thick film were not well controlled this time; we believe that more oriented films can be obtained in optimized conditions.

CONCLUSION

We observed TH power in DCH-PDA films as a function of the fundamental waves' incidence angles in internal reflection geometry and obtained the ratio of their $\chi^{(3)}$s. The oriented LB film of poly(3BCMU) under the DCH-PDA film contributed to polymer-orientations in the DCH-PDA film. The $\chi^{(3)}$of DCH-PDA film deposited on the LB film was enhanced by a factor of 2.1 because of the partial orientation.

It is difficult to apply the transmission type THG measurements like Maker-fringe technique, to some thick films because of their strong absorbance and optical roughness. Using the reflection mode provides TH signals regardless of the strong absorption of the sample. The interface between a film and a substrate often has better quality than surface of another side. Internal reflection type experiments are more suitable for films for which smooth surfaces are hard to obtain. Scatter effects could be approximately taken into account using complex refractive indices.

Sample refractive indices at ω and 3ω were obtained as fitting parameters. In order to measure the complex refractive index of samples at ω, the setup can be easily modified to observe the reflectivity for ω waves by changing the filters before the photomultipliers to ω wave pass filters. The complex refractive index at 3ω can be measured using incident 3ω waves. Film thickness is also obtained by these measurements. This technique has an advantage for inhomogeneous samples, because

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$\chi^{(3)}$, film thickness and refractive indices at the same point are obtained in the same arrangement.

This technique has the potential to provide a $\chi^{(3)}$ distribution in the direction of thickness for transparent films, because the penetration depth of evanescent waves can be varied by changing the incidence angle. It provides some information about molecular orientation. As the TH signal is proportional to the cube of the incidence power, we expect that it has a higher resolution than linear measurements like ATR. Moreover, this technique can be applied to poled polymer films for SHG.

ACKNOWLEDGMENT

The authors thank Mr. Tatsuya Uzuka and Mr. Hiroshi Eguchi of Japan Laser Corp. for the loan of the BMI laser system. We would like to acknowledge Dr. Yasushi Tomioka for his help in creating LB films.

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