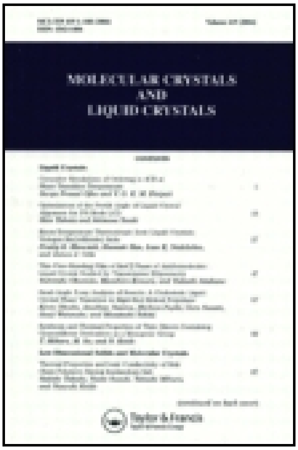

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Recent Improvement in the Surface Analysis Method Using Surface Second-Harmonic Generation

Takahiro Sakai [a], Byoungchoo Park [a], Jeong-Geun Yoo [a], Hajime Hoshi [a], Ken Ishikawa [a] & Hideo Takezoe [a]

[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

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TAKAHIRO SAKAI, BYOUNGCHOO PARK, JEONG-GEUN YOO, HAJIME HOSHI, KEN ISHIKAWA AND HIDEO TAKEZOE
Department of Organic and Polymeric Materials,
Tokyo Institute of Technology, O-okayama, Meguro-ku,
Tokyo 152-8552, Japan

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Recent improvement in analyzing molecular orientational distribution function (ODF) at surfaces and interfaces using surface second-harmonic generation (SHG) was reviewed. The anisotropic dielectric constants of SHG-active thin layers were treated as parameters governed by ODF to be determined. The information about the nonpolar axial ordering was added when using the maximum entropy method for analyzing ODF. Importance of the imaginary part of nonlinear susceptibility elements was also pointed out. A spin-coated film of polyimide with SHG-active side chains was chosen as an example and ODFs of the rubbed surface were obtained with and without using these modified methods for comparison.

Keywords: surface, second-harmonic generation, maximum entropy method

1. INTRODUCTION

Growing attention has been paid to surfaces from the viewpoints of basic science and application. One of the powerful methods for the surface analysis is optical second-harmonic generation (SHG) because of its high sensitivity to surface and interfaces. This technique has been successfully applied to many surfaces particularly by Shen and his coworkers[1] giving us a lot of knowledge about surface, such as molecular orientational distribution functions (ODFs). In spite of their pioneering works, however, there are still many problems to be solved. They are:

(1) The dielectric constant of an SHG active layer was not properly chosen. For instance, Feller et al.[2] assumed that the dielectric constant of an SHG active layer is the same as that of air and many researchers follow this

assumption. Of course, it is not true. Strictly speaking, the dielectric constant is not a scalar but anisotropic and depends on ODF.

(2) In $C_{\infty v}$ symmetry, only the ratio of two nonlinear susceptibility elements χ_{zxx}/χ_{zzz} can be determined. Therefore, one have to assume a width of ODF to determine an average tilt angle, even if the Gaussian distribution is assumed[1]. Moreover, the choice of the width seriously influences the resultant average tilt angle[3].

(3) In C_{1v} symmetry, six nonzero χ elements could be determined by appropriate surface SHG experiments, providing information about the first- and third-order Legendre polynomials, but not the second-order one. Because of the lack of information of $<\cos^2\theta>$, erroneous ODFs were sometimes obtained when using the maximum entropy method[4].

(4) Most of the experiments were performed under a resonance condition to enhance SHG signal intensity. However, the Kleinmann symmetry was almost always assumed. Moreover, the imaginary part of χ was neglected.

In this paper, modified analysis methods so far we developed were reviewed. These modified methods were applied to a spin-coated film of polyimide with SHG-active side chains and ODFs were obtained with and without using these modified methods for comparison.

2. MODIFIED ANALYSIS METHODS

Determination of Anisotropic Dielectric Constants of SHG-Active Layers

The choice of the appropriate dielectric constants of SHG-active layer is very important for reliable analysis, since dielectric constants give local field factors and boundary conditions of light field at interfaces. Generally, however, it is very difficult to determine the dielectric constant of SHG-active layers, since the layers are usually a single molecular thickness and anisotropic. The dielectric constant in thin films must be different from that in the bulk. Moreover, it depends on ODF to be determined. Therefore, the dielectric constants should be described by

$$\varepsilon_{ii} = n_{ii}^2 = 1 + \frac{(n_e^2 - 1)}{3}(2S_{ii} + 1) + \frac{(n_o^2 - 1)}{3}(2 - 2S_{ii}), \quad (1)$$

where n_o and n_e are the ordinary and extraordinary refractive indices for the perfect ordering, respectively, and

$$S_{zz} = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle , \tag{2}$$

$$S_{xx} = \frac{1}{2}\langle 3(1 - \cos^2\theta)\cos^2\phi - 1\rangle , \tag{3}$$

$$S_{yy} = \frac{1}{2}\langle 3(1 - \cos^2\theta)\sin^2\phi - 1\rangle , \tag{4}$$

where <···> means the molecular average under ODF. In this way, the problem (1) could be solved[5].

Modified Maximum Entropy Method

In order to determine ODF, the maximum entropy method has been used[4]. In this method, the information entropy defined by

$$H(f(\theta,\phi)) = -\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} f(\theta,\phi)\ln f(\theta,\phi)d\phi \tag{5}$$

is maximized under constraint functions f_i. This is equivalent to maximizing the quantity $H - \Sigma\lambda_i f_i$, where λ_i is Lagrange undetermined multipliers. The maximization leads to the distribution function

$$f(\theta,\phi) = \frac{\exp[\Sigma\lambda_i f_i]}{\iint \exp[\Sigma\lambda_i f_i] \sin\theta d\theta\, d\phi} . \tag{6}$$

There are six constraint functions

$$f_1 = \cos^3\theta \tag{7}$$

$$f_2 = \sin^3\theta\cos^3\phi \tag{8}$$

$$f_3 = (\cos\theta - \cos^3\theta)(1 - \cos^2\phi) \tag{9}$$

$$f_4 = (\cos\theta - \cos^3\theta)\cos^2\phi \tag{10}$$

$$f_5 = (\sin\theta - \sin^3\theta)\cos\phi \tag{11}$$

$$f_6 = \sin^3\theta(\cos\phi - \cos^3\phi) \tag{12}$$

Here f_is (i=1~6) are related to χ_{zzz}, χ_{xxx}, χ_{zyy}, χ_{zxx}, χ_{zxz} and χ_{xyy}, respectively. It is noted that there is no information of $\cos^2\theta$ in f_is, which sometimes leads to erroneous ODFs. In our modified maximum entropy method[6], we add an additional constraint function

$$f_7 = \cos^2\theta. \tag{13}$$

Combined Analysis Method

By combining the improvement mentioned in 2.1 and 2.2, we can determined unbiased ODF[7]. Figure 1 shows a flow chart of the present analysis. First, by tentatively choosing Lagrange undetermined multipliers λ_i, a tentative ODF could be obtained by using the modified maximum entropy method, in which eq. (6) is used with seven constraints functions, eqs. (7)~(13). The ODF gives the anisotropic dielectric constants through eqs. (1)~(4). The theoretical SH-light intensities in different geometries can be calculated by using these values and taking account of the appropriate local field factors at interfaces. For the analysis of a spin-coated polymer film, the five layer model was used[5]. By finding the best fit of this intensities with the experimental results measured in several optical geometries, we can determine λ_i and obtain the final ODF. This final ODF provides S_{ii} through eqs. (2)~(4) and ε_{ii} through eq. (1). The ratio of six χ elements is also obtained by averaging eqs. (7)~(12) under ODF obtained.

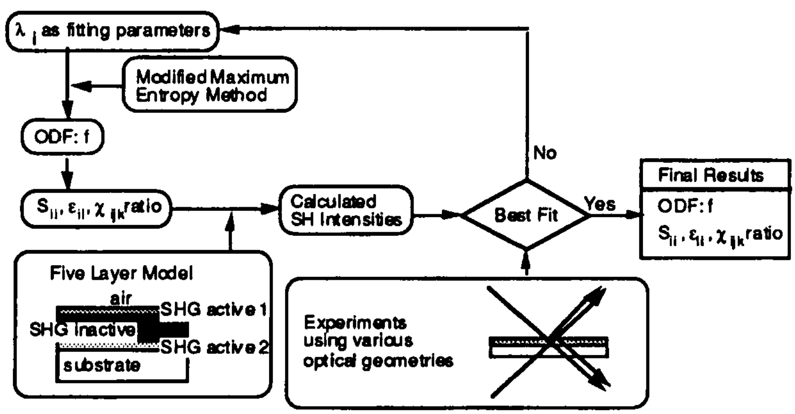

FIGURE 1 Flow chart of the improved analysis method.

Further Improvement

Using the improvement mentioned above, the problems (1)~(3) can be solved. For the problem (4), we recently proposed a method of determining all the complex χ elements without using the Kleinmann symmetry[8]. In this method using a rotating quarter wave plate, better fitting result was obtained when using complex χs than that obtained by assuming real χs. The obtained ODF also differs seriously. The details will be reported elsewhere[8].

3. EXPERIMENTAL RESULTS AND DISCUSSION

As an example for the present improved analysis method, a rubbed film of polyimide with SHG-active side chains was examined. The sample and the experimental method were described in our previous papers[5-7]. The SH-light intensities as a function of sample rotation angle about its surface normal are shown in Fig. 2. Anisotropic (closed symbols) and isotropic (open symbols) signals were observed using four polarization combinations; *p-p*, *s-p*, *p-s*, and *s-s*, where *s-p* means *s*-in and *p*-out.

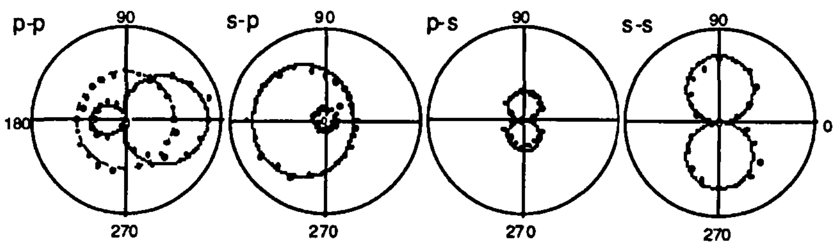

FIGURE 2 SHG intensity an a function of sample rotation angle in reflection (closed symbols) and transmission (open symbols) directions, from which a rubbed air-polymer surface and a polymer-substrate interface can be assessed.

The conventional and the modified maximum entropy methods were applied to determine ODF of the rubbed surface. The contour maps are shown in Fig. 3. The brighter part represents the higher distribution of the side chains. The difference particularly in the existence and the absence of a peak around 180° should be noticed. The peak is an artifact caused by the lack of information of the nonpolar axial ordering.

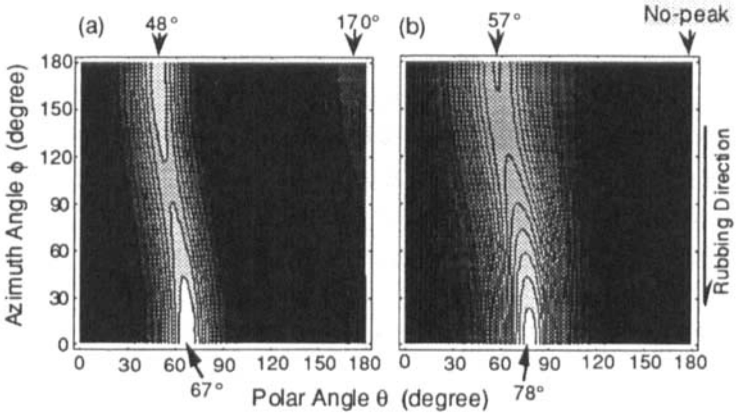

FIGURE 3 Contour maps of the ODF of the SHG-active side chains obtained using (a) conventional and (b) modified maximum entropy methods.

4. CONCLUSION

After summarizing the problems to be solved for the analysis of ODFs using surface SHG and the maximum entropy method, recent development in the improved analysis methods was described. An example was shown to emphasize the difference between the conventional and the modified methods.

References

[1.] Y. R. Shen, *Annu. Rev. Phys. Chem.*, **40**, 327 (1989).
[2.] M. B. Feller, W. Chen and Y. R. Shen, *Phys. Rev.*, **43**, 6778 (1992).
[3.] H. Takezoe and K. Kajikawa, *Mol. Cryst. Liq. Cryst.*, **227**, 93 (1993).
[4.] B. Jerome and Y. R. Shen, *Phys. Rev.*, **E48**, 4556 (1993).
[5.] J.-G. Yoo, H. Hoshi, T. Sakai, K. Ishikawa, H. Takezoe and Y. S. Lee, *J. Appl Phys.*, submitted.
[6.] B. Park, Y. Kinoshita, T. Sakai, Y.-G. Yoo, H. Hoshi, K. Ishikawa and H. Takezoe, *Phys. Rev.* E., in press.
[7.] J.-G. Yoo, B. Park, T. Sakai, Y. Kinoshita, H. Hoshi, K. Ishikawa and H. Takezoe, *Jpn. J. Appl. Phys.*, in press.
[8.] B. Park, J.-G. Yoo, T. Sakai, H. Hoshi, K. Ishikawa and H. Takezoe, *Phys. Rev.*, E, submitted.