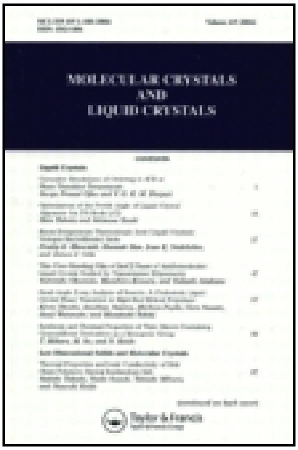

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Determination of Orientational Distribution of Side Chains of Polyimide Layer for Liquid Crystal Alignment by Surface Second-Harmonic Generation

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Determination of Orientational Distribution of Side Chains of Polyimide Layer for Liquid Crystal Alignment by Surface Second-Harmonic Generation

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We have determined the orientational distribution function (ODF) of the side chain polyimide (PI) films used for liquid crystal alignment. The second-harmonic generation (SHG) in four sample geometries were measured as a function of polarizer rotation angle. To determine ODF, we developed a new fitting method of the five layer model using the maximum entropy method. We found that the ODF of the side chains of PI film of the air-side surface is quite different from that of the substrate side.

Keywords: second-harmonic generation, polyimide, liquid crystal, orientational distribution function, information entropy, maximum entropy method

INTRODUCTION

The determination of orientational distribution function (ODF) of organic functional groups at interfaces is of not only scientific interest but also technological importance for various devices such as liquid crystal (LC) displays. For the interfacial study, the optical second-harmonic generation (SHG) technique has become a powerful tool[1]. Using this technique, the LC monolayers on various surfaces have already been studied[2,3]. However, the polymer surface used for the LC alignment has not been studied sufficiently.

In this report, we propose a method to determine ODF in $C_{\infty v}$ symmetry using a five-layer model and the maximum entropy method[4,5]. We show the ODFs of side chains at both interfaces of a polyimide film.

EXPERIMENTAL

The polymer used was polyimide (PI) with cyanobiphenyl-substituted side chains, which give rise to SHG activity, as shown in Fig. 1. A PI film was prepared by spin coating on a clean fused quartz substrate. The details for the surface SHG measurement were as previously described[5]. The PI film was irradiated by 532 nm fundamental beam at an incident angle of 45°. The *p*-polarized SHG (266 nm) was observed as a function of polarizer rotation angle from 0°(*p*) to 90°(*s*) in four geometries shown in Fig.1.

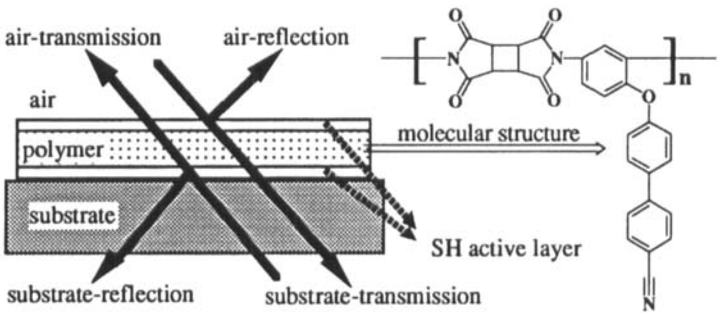

FIGURE 1. Sample geometry for SHG measurement.

RESULTS AND DISCUSSION

Although the present PI has SHG active side chains, the spin-coated PI film is isotropic. Hence, the bulk does not emit SHG signal. However, the side chain of the PI at the interfaces between the PI film and the air or the substrate can emit SHG light because of polar orientations of side chains[6]. Note that the both interfaces contribute to SHG observed in all four geometries. We describe the PI film as a five-layered system consisting of (1) air, (2) SHG active PI surface layer of the air side, (3) SHG inactive PI bulk film, (4) SHG active PI surface layer of the substrate side and (5) substrate. In all layers, the tangential (x) components of the wave vector are all the same, but the normal (z) component of the wave vector depends on the dielectric constant of each layer. In this model, we also considered that the dielectric constant of the SHG active layer depends on the distribution of side chains. Including appropriate Fresnel factors in this model, one can calculate the exact local field factors and find the theoretical transmitted or reflected SHG light intensities.

Figure 2 shows the *p*-polarized SHG light intensities observed in four sample geometries as the function of polarizer rotation angle. The solid curves are the best fit obtained from one set of parameters according to the following procedure. First, we assumed that the side chains at the interfaces have $C_{\infty v}$ symmetry and there are only two NLO components χ_{zzz} and χ_{zii}, where i = x and y. Then assigning certain undetermined multipliers in the maximum entropy method[4,5], we obtained temporary ODFs for two SHG active layers. With these ODFs, we obtained NLO coefficients and the dielectric constants of the active layers followed by the calculation of the local field factor using the dielectric constants determined. From this local filed factor and NLO coefficients, we calculated the SHG intensities from the five layers. The calculated result was compared with the experimental results shown in Fig. 2, using the undetermined multipliers as fitting parameters. From the best fit, we can determine the true ODFs. The details of the calculation will be reported in a separate paper. As shown in Fig. 2, it is clear that our five-layer model explains the experimental result very well. From the fitting procedure, we

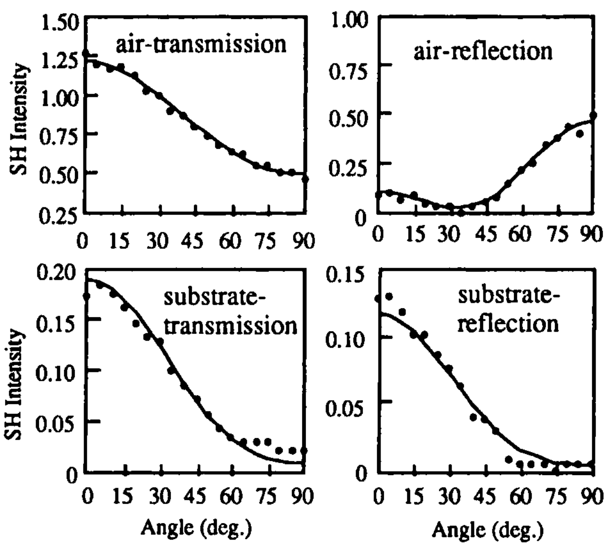

FIGURE 2. Experimental (dots) and simulated (solid curves) *p*-polarized SHG intensities as a function of polarizer rotation angle.

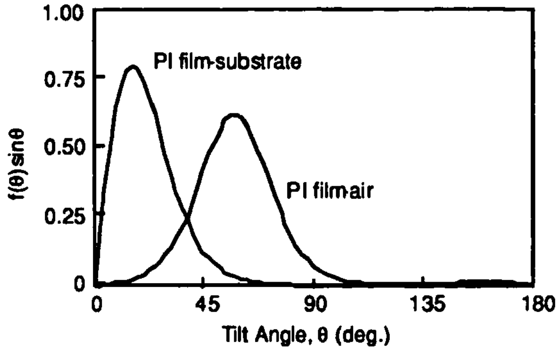

FIGURE 3. ODFs of side chains at the two interfaces.

obtained χ_{zzz}/χ_{zxx} = 1.27 at the substrate-film interface and χ_{zzz}/χ_{zxx} =11.0 at the air-film interface. The ODFs, f(θ), multiplied by sinθ are plotted in Fig. 3. The angles of the maximum distribution of the side chains on the air-film and the substrate-film interfaces are found to be about 58° and 16°, respectively, implying that the side chains of PI at the interface between substrate and film are more highly ordered than those at the interface between air and film.

In conclusion, we considered a polymer film as a five-layered system including two SHG active layers at the both interfaces. Using the five-layer model, we calculated the theoretical SHG intensities with the appropriate local field factors at each layer. Using the observed SHG signal from the side chain PI film, we obtained the nonlinear coefficients and the orientational distribution functions of air-film and substrate-film interfaces. From these results, it was found that the side chains of PI at the interface between substrate and film are more highly ordered than those at the interface between air and film.

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