

Title	ポリイミド表面のステロイド構造側鎖の和周波発生振動分光法
Author(s)	NGUYEN, Thi Trinh
Citation	
Issue Date	2021-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/17529
Rights	
Description	Supervisor:水谷 五郎, 先端科学技術研究科, 博士

Sum frequency generation vibrational spectroscopy of steroidal structure side chains of polyimide surfaces

Doctor of Philosophy (Materials Science)

Mizutani Laboratory

1820406

Nguyen Thi Trinh

Polyimide (PI) films for coating glass substrate are commonly used to align the liquid crystal (LC) molecules in liquid crystal display (LCD) devices. Among them, PI containing steroidal side chains, as shown in Fig.1, is expected to be useful because it provides a wide range of pretilt angles according to its diamine ratio. Unfortunately, the orientation and conformation of molecules at the PI surface after rubbing have not been fully known yet so far, especially so far as a steroidal structure and alkyl chain parts are concerned.

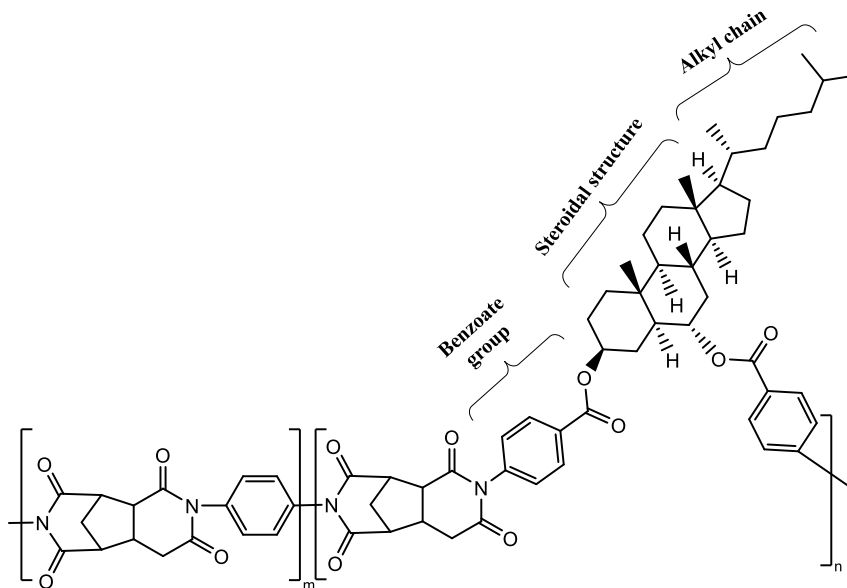


Figure 1. Chemical structure of PI containing steroidal side chains used in this study.

Ullah *et al.* reported that the second harmonic generation (SHG) intensity of a rubbed PI film with units possessing a 30% fraction of steroidal side chains (PI-30) shows anisotropic SHG intensity patterns as a function of the sample rotation angle. To analyze the experimental result, they assumed that only the steroidal side chains of the PI-30 have microscopic optical nonlinearity. However, Ullah *et al.* have not checked the validity of the assumption yet. In this study, I first observed SHG response from unrubbed PI film surfaces at several different molar fractions of side-

chain diamine in PI containing steroidal side chains, PI-0, PI-30, PI-60, PI-90, and PI-100, to examine whether or not their assumption was correct. I found that both the PI main chains and PI side chains contribute similarly to the SHG intensity. The SHG intensity in S_{in}/P_{out} polarization configuration normalized by P_{in}/P_{out} was the smallest for the unrubbed PI-0 film, or the PI without steroidal side chains. This fact indicates that the microscopic nonlinear dipoles are standing nearly upright at the surface of the unrubbed PI-0 film. In contrast, their orientational spread is wider when the side chains are involved.

The molecular orientation of steroidal side chains at the rubbed PI surfaces was investigated by sum frequency generation (SFG) vibrational spectroscopy to establish a correlation between the molecular structure and LC alignment. Several analytical techniques are used to study polymer films, such as infrared spectroscopy, atomic force microscopy, and near-edge X-ray absorption fine structure spectroscopy. However, they are not helpful for analyzing the steroidal structure and the alkyl chain parts. On the other hand, SFG vibrational spectroscopy has been demonstrated as a useful surface analytical technique. Because this technique is sensitive to non-centrosymmetric parts of materials, it is commonly used to determine vibrational resonances of molecules adsorbed at surfaces and interfaces.

In SFG measurements, I have investigated three types of PI-30 films, including unrubbed PI-30 film, rubbed PI-30 film, and rubbed PI-30 film with a poly (methyl methacrylate) (PMMA) overlayer. Before analyzing the details of the SFG spectra of the PI-30 film, I examine whether or not the SFG response originates from the PI-30 film surface. For this purpose, I measured the SFG spectra of the rubbed PI-30 films with and without a PMMA layer for PPP and SSP polarization combinations. The thickness of the PMMA layer was ~ 5 nm. The SFG intensity decreased dramatically after the sample was covered with the very thin PMMA layer for the PPP polarization combination. Furthermore, the peaks in the spectra changed drastically after PMMA deposition for the SSP polarization combination. These results indicate that the SFG of the rubbed PI-30 film mainly originates from the PI film surface, and the SFG contribution from the PI/glass substrate interface and the bulk PI can be ignored.

In the SFG spectrum of the rubbed PI-30 film in the CH stretching region from 2800 to 3000 cm^{-1} at an azimuthal angle of $\gamma = 0^\circ$ and for a PPP (P-polarized SFG, P-polarized visible, P-polarized IR) polarization combination, I found that the frequencies of the symmetric and antisymmetric stretches of the CH_3 groups at the end of the alkyl chain are different from those of the two CH_3 groups on the steroidal structure and the adjacent CH_3 group.

To analyze the effect of the rubbing process on the orientation of the CH_3 groups at the PI side chain, I focus on the CH_3 symmetric stretching modes in 2850-2890 cm^{-1} region. The SFG spectra

of the rubbed PI-30 film at azimuthal-angle intervals of 45° for a PPP polarization combination were observed. The spectra showed that the isopropyl group is pointing toward the air side from the PI surface, but their average orientation is not affected by rubbing because the length of the alkyl chain in this PI is short. However, a slight anisotropy of the symmetric stretching mode of the CH_3 group next to the steroidal structure was observed in the SFG spectra after rubbing. Its average tilt angle was estimated as $\theta_0 = 40^\circ \pm 10^\circ$ in the rubbing direction. These results indicate that the rubbing appears to cause conformational changes of the CH_3 group near the steroidal structure, but the rubbing does not significantly affect the orientation of the isopropyl group at the end of the PI side chain.

The correlation between the molecular orientation at the surface of the PI containing steroidal side chains and the alignment of LC molecules on this rubbed PI film is important from a scientific perspective. It is also desirable from an industrial perspective because it helps to understand the mechanism of LC alignment on the rubbed polymer surface and provides a reference for the design of new PI containing steroidal side chains for future commercial research in the display industry. Nevertheless, to the best of my knowledge, there is no study investigating the molecular orientation and conformation of the steroidal structure and the alkyl side chain at the rubbed PI film surface like the one in this study. Hence, it is unknown yet which part of the rubbed PI film containing steroidal side chains is most strongly correlated with LC alignment. Therefore, the ultimate purpose of my study was to establish which structural factor of rubbed PI films with steroidal side chains is most strongly correlated with LC alignment.

There are three possible structural factors were considered: (1) the phenyl rings, (2) the steroidal structure and the adjacent CH_3 group, and (3) the isopropyl group and the neighboring methylene group in the PI side chain. Among them, factor (3) can be excluded because it does not show any anisotropy after rubbing. Consequently, only two factors (1) and (2) are possibly correlated with LC alignment. Unfortunately, I cannot determine so far which of them is mainly related to LC alignment, and further study is necessary for resolving this issue.

Keywords: polyimide, sum frequency generation vibrational spectroscopy, molecular orientation, alignment layer, and steroidal structure.