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論文題目	Sum frequency generation vibrational spectroscopy of steroidal structure side chains of polyimide surfaces
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論文の内容の要旨

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.

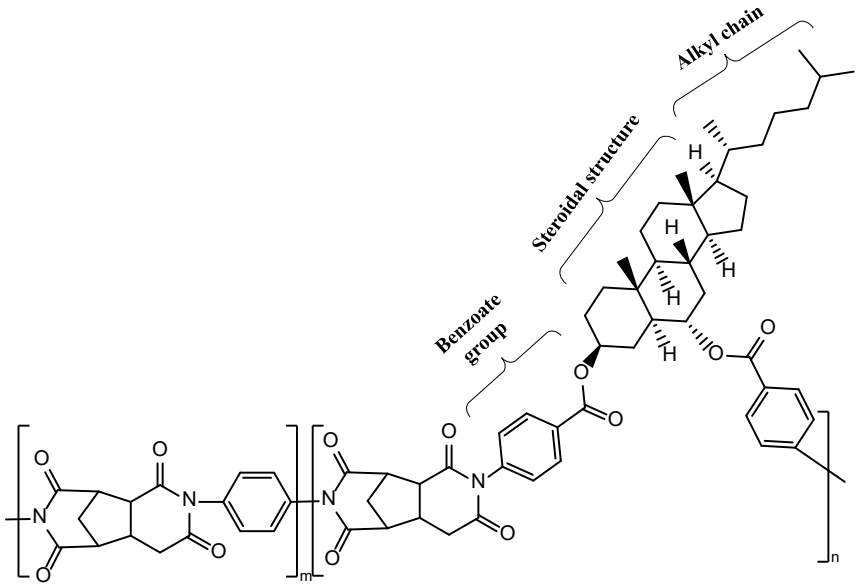

Figure 1. Chemical structure of PI containing steroidal side chains used in this study.

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 $\gamma = 0^o$ 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^o 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 $\theta_0 = 40^o \pm 10^o$ 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.

論文審査の結果の要旨

本論文では、液晶パネルの液晶分子を配向させるステロイド構造を持つポリイミド膜基板の最表層の構造の情報を二次の非線形光学分光法(光第二高調波分光:SHG、光和周波分光:SFG)を組み合わせて分析し、最表層の部位のラビングによる構造変化を検出した。

ポリイミド膜試料は産学共同研究により JSR 株式会社と作成した。試料の構造はガラス基板/ITO/ポリイミド膜であり、厚さ 80nm のポリイミド膜はスピンコーティングで形成した。ステロイド構造を含むジアミンによる側鎖を０～１００％の割合で導入した。なお、ジアミン比３０％のポリイミド基板はラビングにより液晶層の分子を配向させることがわかっている。試料のラビングはナイロンのローラを用いて行った。二次の非線形現象の応答が試料の最表面で起きていることを確認する実験のためには、スピンコーティングで試料上に厚さ 5nm の PMMA 膜を形成した。

非線形光学計測は、パルス時間幅 30ps、繰り返し周波数 10Hz の Nd:YAG レーザーの二倍波(光子エネ

ルギー2.33eV)を光源として用い、SHG 計測では試料による反射方向に発生する SHG 光を分光器を通して光電子増倍管で計測し、SFG 計測ではさらに光パラメトリック発振器により発生する赤外光を同時に入射して、発生する SFG 光を同様に計測した。主たる計測に先立って、厚さ 5nm の PMMA の被覆の有無による試料の SFG スペクトルの違いにより、SFG 光シグナルがポリイミド膜の最表面から出ていることを確認した。また乾燥窒素中に保持した試料との比較により、試料は環境がコントロールされた実験室の大気中で３か月程度安定であることが確認できたので、測定はその期間内に行った。

ステロイド構造を含むポリイミド膜の化学構造には、CH_3 基が側鎖の末端のイソプロピル基の中に２つ、ステロイド構造の周辺に３つある。試料の SFG スペクトルではこれらの CH_3 基の振動を区別して検出することができた。この SFG シグナルと SHG シグナルを用い、配向膜上の液晶層の配向に対する配向膜のラビングの影響に関わっている構造的要因として３つの候補、すなわち(1)ポリイミド鎖中の芳香族環、(2) ステロイド構造、(3) 側鎖のイソプロピル基、をチェックした。まず(1)については文献によりジアミン比率３０％の試料についてラビングの影響があることがわかった。(2)については、本研究の SFG シグナルによりラビングにより異方性が発生することがわかった。そして、ステロイド構造に隣接する CH_3 基の試料法線に対してなす角度を 40 ± 10^{o} と評価した。(3)のイソプロピル基は、ラビングを施した試料の SFG シグナルが試料回転角依存性をもたないことから候補から除外した。従って(1)と(2)を液晶層の配向に関連している主たる要因として提案した。

以上、本論文におけるこれらの成果は、液晶パネル材料の新たな非線形光学的解析法の応用例として、学術的にもまたデバイス技術などへの将来の応用にも貢献するところが大きい。よって博士(マテリアルサイエンス)の学位論文として十分価値あるものと認めた。