EPITAXIAL GROWTH OF POLYDIACETYLE THIN FILMS
AND THEIR NONLINEAR OPTICAL PROPERTIES

Y. HATTORI, A. MIZOGUCHI, and A. NISHIMURA
New Chemistry R&D Laboratories,
Sumitomo Electric Industries, LTD.
1-1-3, Shimaya, Konohana-ku, Osaka, 554 JAPAN

PDA-3BCMU monomer was epitaxially grown on KCl substrate by vacuum-deposition method. Followed by solid phase polymerization, the PDA-3BCMU thin film containing square crystals was obtained. The PDA main chains in the crystals were parallel to KCl[110] or [110] direction. THG anisotropy of the thin film was explained by the orientation of PDA main chains and enhancement of $\chi^{(3)}_{\text{THG}}$ was observed against un-oriented PDA-3BCMU thin film.

1. Introduction

Polydiacetylenes (PDAs) have attracted considerable interest because of their large nonlinear optical (NLO) properties and fast response time due to their $\pi$-conjugated main chains [1-2]. Therefore PDAs are expected to be applied in all optical switching devices which consist of polymer waveguides. The molecular orientation control of the PDAs is important for the fabrication of the PDA thin film waveguides to optimize the interaction between the polymers and pumping laser light.

In this paper, we report the orientation control of poly(4,6-decadiyne-1,10-diol-bis(n-butoxycarbonylmethylurethane))(PDA-3BCMU) which can be obtained by solid phase polymerization of monomer crystal [3]. The orientation control was carried out by vapor phase epitaxy of its monomer on KCl substrates and its polymerization. Anisotropy of third harmonic generation (THG) and nonlinear susceptibility, $\chi^{(3)}_{\text{THG}}$, are also measured and are discussed with the orientation of PDA main chains.

2. Experimental

PDA-3BCMU monomer was vacuum-deposited on KCl substrate under the pressure of $3 \times 10^{-5}$ torr. KCl substrates were cleaved from KCl single crystal.
and were heated at 150°C for 30 min. in a vacuum chamber before the deposition. The deposition condition was controlled between -10°C and 50°C for substrate temperature and between 0.5Å/min. and a few hundred Å/min. for deposition rate. The deposition rate and thickness of the thin film were monitored by a quartz oscillator microbalance. The monomer thin films were polymerized by UV light (254nm) irradiation with monitoring UV-VIS optical spectra to avoid decomposition.

Morphology of the thin films was observed with an optical microscope and a transmission electron microscope. Molecular orientation was determined from electron diffraction patterns. THG anisotropy and THG Maker fringe were measured with Nd:YAG laser, dye laser and difference frequency generator system for pumping light source and photomultiplier, Boxcar averager and personal computer system for TH signal detection. Wavelength, pulse energy and pulse width of pumping laser light were 1.9μm, 3mJ and 6ns, respectively.

3. Result and Discussion
3.1 Orientation Control of PDA-3BCMU thin films

The morphologies of PDA-3BCMU monomer thin films varying the deposition condition are shown in Fig.1. The monomer thin films were amorphous or droplet under almost all of deposition conditions, but monomer crystals were grown epitaxially only at high substrate temperature and slow deposition rate as shown in Fig.1(d). The monomer crystals were about 3x3μm square which direction were parallel to the KCl[110] and [110] direction as shown in Fig.2(a). The amorphous area was also observed between the square crystals.

As shown in Fig.2(b), the electron diffraction pattern of the square crystal was found as a single crystal pattern and was interpreted using crystal parameters of bulk PDA-3BCMU monomer crystal. The monomer molecules were perpendicular to the substrate surface as shown in Fig.3(a) and were stacking along the KCl [110] or [110] direction in each crystal as shown in Fig.3(b).

Following the epitaxial growth, the monomer thin film was polymerized by UV light irradiation. The irradiation caused increase of absorption around 630nm and the monomer thin film turned into a blue polymer thin film. The electron diffraction pattern of polymerized crystal was similar to that of the monomer crystal except for a small difference of lattice spacings. An observation by cross polarized microscope showed that the PDA-3BCMU main chains in
the crystals were parallel to the KCl[110] or [1$ar{1}$0] direction corresponding to the stacking direction of monomer molecules. These results showed that monomer...
molecules were polymerized without changing their orientation, therefore the orientation of PDA main chains was controlled by the epitaxial growth of the monomers.

On the other hand, the electron diffraction pattern of the amorphous area between the square crystals was a halo pattern before polymerization. However, this area was also polymerized. These results suggested that monomer molecules might have a stacking structure in very short range but they were random to each other in longer range. After the polymerization, therefore, the PDA main chains in this area had a random orientation (un-oriented). Though the square crystals became larger with the progress of the deposition, this un-oriented area remained at any stage as the thin film shown in Fig.4, which thickness was 1750Å, 6 times larger than that of the thin film shown in Fig.2(a). THG measurement mentioned below was performed on this PDA-3BCMU thin film.

Fig.3 (a) Molecular orientation and (b) stacking direction of PDA-3BCMU monomers

Fig.4 Electron micrograph of PDA-3BCMU thin film (1750Å)
3.2 THG properties of PDA-3BCMU thin films

THG anisotropy was measured with the experimental configuration as shown in Fig.5. The incident direction of linear polarized pumping laser light was perpendicular to the thin films. With rotating the thin film around the incident direction, TH signal was detected through an analyzer which polarization direction was parallel to that of pumping laser light. TH intensity of the PDA-3BCMU thin film is shown as the closed circles in Fig.6. It shows two peaks at 45° and 135°, where the PDA main chains of the crystals and polarization direction of the pumping laser light were parallel to each other.
In the case of conjugated polymers such as PDAs, a $\chi^{(3)}$ tensor component along polymer main chain contributes dominantly to THG because it is 100 times larger than the other components[4]. Therefore, TH intensity for PDA single crystal is proportional to $(\cos^4\psi)^2$, where $\psi$ is the angle between PDA main chain and the polarization direction of pumping laser light[5]. As mentioned before, the PDA-3BCMU thin film consisted of oriented crystal part and un-oriented part. Therefore, TH intensity of the PDA-3BCMU thin film is expressed by the summation of the electric field of TH from each parts as below.

$$I_{3\omega} = |\alpha E_{3\omega}(\text{ori.}) + (1-\alpha)E_{3\omega}(\text{un-ori.})|^2$$  \hspace{1cm} \text{eq.1}

where $I_{3\omega}$ is TH intensity. $E_{3\omega}(\text{ori.})$ and $E_{3\omega}(\text{un-ori.})$ are electric field of TH from oriented and un-oriented parts, respectively. $\alpha$ is the ratio of the oriented part. In the oriented part, it could be assumed that half of PDA main chains were parallel to KCl[110] and the another half were parallel to KCl[110]. Therefore $E_{3\omega}(\text{ori.})$ and $E_{3\omega}(\text{un-ori.})$ are expressed as below.

$$E_{3\omega}(\text{ori.}) = A*0.5*[0.5*\cos^4\theta + 0.5*\cos^4(\theta + 90^\circ)]*\chi^{(3)}_{1111}E_{\omega}$$  \hspace{1cm} \text{eq.2}

$$E_{3\omega}(\text{un-ori.}) = A*[\cos^4\psi]*\chi^{(3)}_{1111}E_{\omega}$$  \hspace{1cm} \text{eq.3}

where $E_{\omega}$ is electric field of pumping laser light and $\chi^{(3)}_{1111}$ is a $\chi^{(3)}$ tensor component of PDA single crystal along its main chain. $A$ is a constant depending on experimental conditions. $\theta$ is rotation angle($\theta=0^\circ$ when polarization direction is parallel to KCl[100] direction). The solid line in Fig.6 is the best fit curve of the eq.1 which was obtained with $\alpha = 0.79$. From this result, the ratio of oriented part was determined as about 79% in the PDA-3BCMU thin film. The effective susceptibility $\chi^{(3)}_{\text{eff}}$ was estimated as 0.44 times of $\chi^{(3)}_{1111}$ from putting $\alpha = 0.79$, $\langle\cos^4\psi\rangle = 0.2$ and $\theta = 45^\circ$ into eq.1-3. The $\chi^{(3)}_{\text{eff}}$ for un-oriented thin film was 0.2 times of $\chi^{(3)}_{1111}$ from putting $\alpha = 0$ into eq.1-3. Therefore, the $\chi^{(3)}_{\text{eff}}$ ratio of the PDA-3BCMU thin film to an un-oriented one was $0.44/0.2 = 2.2$.

THG Maker fringe method was applied to evaluate $\chi^{(3)}_{\text{THG}}$ of the PDA-3BCMU thin films. The evaluation was made according to the procedure S. Tomaru et al reported[6]. $\chi^{(3)}_{\text{THG}}$ of un-oriented thin film deposited on fused silica and the oriented PDA-3BCMU thin film were $0.7\times10^{-10}$ esu and $1.5\times10^{-10}$ esu, respectively. The $\chi^{(3)}_{\text{THG}}$ ratio of the PDA-3BCMU thin film to an un-oriented one was about 2.1 and it was found to be in very good agreement with the $\chi^{(3)}_{\text{eff}}$ ratio, 2.2, estimated from THG anisotropy. This good agreement indicates that the orientation control of PDA main chains effects $\chi^{(3)}_{\text{enhance-}}$
ment directly.

4. Conclusion

Molecular orientation controlled PDA–3BCMU thin film was obtained by vapor phase epitaxy of the monomer on KCl substrate and its solid phase polymerization. The thin film consisted of un-oriented part and oriented part in which PDA main chains were parallel to KCl[110] or [110] direction. THG anisotropy and the enhancement of $\chi^{(3)}_{\text{THG}}$ were explained from the **rate** of oriented part. These results indicates the importance of the molecular orientation control for the fabrication of PDA thin film waveguides.

Acknowledgment

This work was performed by Sumitomo Electric Industries, LTD. under the management of the Japan High Polymer Center as a part of the Industrial Science and Technology Frontier Program supported by the new Energy and Industrial Technology Development Organization.

Reference