

Thin Films of Acetalized Poly(vinyl alcohol) as Nonlinear Optical Materials

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ABSTRACT: Acetalized poly(vinyl alcohol)s (PVA) having pendant nonlinear optically (NLO) active groups were synthesized in order to investigate second harmonic generation (SHG) by using two types of poling methods of NLO active moieties; namely, one was Langmuir-Blodgett (LB) orientation and the other was electric field (EF) poling. It was found that the new polymers having pendant NLO active groups showed sharp surface pressure-area (π -A) curves to form thin films on the surface of water but no active SHG was observed. On the other hand, the polymer films with a support of stearamide showed a SHG activity. When the new polymers were EF poled using corona poling method, SHG was also observed and the SHG activity was estimated as 40.8 pm V^{-1} . The new NLO polymers poled by the EF method showed small SHG relaxation and were useful as a new type SHG material.

KEY WORDS Acetalized Poly(vinyl alcohol) / Nonlinear Optical Property / Second Harmonic Generation / Langmuir-Blodgett Orientation / Corona Electrical Poling / Relaxation /

Recently, organic nonlinear optical (NLO) materials are becoming very important in the field of opto-electronic devices because they have potential applications such as photonic devices. Organic polymers are one of major materials for NLO applications because of their ability to design their molecular structures and their processability to make photonic devices. Main characteristics of NLO polymers are summarized in comparison to those of inorganic compounds as follows;

- (1) Large optical nonlinearities
($> 30 \text{ pm V}^{-1}$)
- (2) Ultrafast response times ($< \text{GHz}$)
- (3) Large induced damage thresholds
($> 10^3 \text{ MW cm}^2$)
- (4) Good processability
- (5) Orientation process is necessary

There would be three different types of

NLO polymers. One is the molecularly doped system which is a physical mixture of polymer and NLO organic compounds.^{1,2} The second is the side chain-attached polymer which contains the NLO moiety as pendant groups by chemical linkage.³⁻⁵ And the third is main chain-type polymer⁸ and cross-linked polymer⁷ containing NLO moieties.

The polymers which have NLO moiety usually do not exhibit SHG activity by itself, because the centrosymmetric structure of NLO moieties cancel the SHG activity. Therefore, orientation of NLO moieties in the polymers is required.

Acetalized poly(vinyl alcohol) can be synthesized easily from poly(vinyl alcohol) (PVA) and aldehyde, and it contains hydrophilic hydroxy groups. This combination of hydrophilic and hydrophobic structures suggest that monolayer films at air/water interface can be

formed. In fact, acetalized PVA having long alkyl chains formed almost perfect monolayer film at air/water interface.⁸ However, the Langmuir–Blodgett (LB) film by vertical deposition was Y-type which has a centrosymmetric structure. In order to attain a high SHG activity, it is necessary to obtain Z-type deposition. Thus, in the present study, mixed monolayer films at air/water interface have been investigated so as to obtain Z-type deposition of the films.

The other orientation method also examined in the present study was an electric field poling. This method is adaptable for side chain-attached polymer especially when the side chain moiety has a strong dipole moment. If the insulation of the polymer was good, the polymer would be effectively poled under the high electric field. The comparison of the two orientation methods of acetalized poly(vinyl alcohol) was made in terms of the SHG activity of the polymer.

EXPERIMENTAL

Synthesis of p-NAn-PVA

Synthetic route is shown in Figure 1.

N-(4-Nitrophenyl)aminoacetaldehyde dimethylacetal. 14.3 g of methylaminoacetaldehyde dimethylacetal (0.12 mol) and 14.11 g of *p*-fluoronitrobenzene (0.1 mol) and 10.08 g of sodium hydrogen carbonate (0.12 mol) and 12 ml of dimethylsulfoxide were mixed and stirred. Heating was continued for 12 hours at 100°C. After the reaction 100 ml of water were added and the solution was extracted 3 times with 50 ml of benzene. The benzene layer was washed with 50 ml of water, 50 ml of aqueous hydrochloric acid solution (0.24 mol l⁻¹), 2 times with 50 ml of water, and dried over anhydrous sodium carbonate. Sodium carbonate was filtered off and the resulting benzene solution was concentrated under vacuum. The residual oil was purified using silica-gel chromatogram. Pale yellow liquid was obtained. 24.0 g (Yield 99%) IR (cm⁻¹); 2900,

1600, 1320, 1110 MS $m/z=240$ (M⁺), 165, 119.

p-NAn-PVA. 0.5 g of PVA having a degree of polymerization of 1500 was dissolved in 35 ml of water at 50°C. 2.1 ml of hydrochloric acid (35% aqueous), 6.00 g of *N*-(4-nitrophenyl)aminoacetaldehyde dimethylacetal (0.025 mol) and 20 ml of methanol was added and stirred for 12 hours at 50°C. The reaction mixture was decanted and residual oil was dissolved in 25 ml of *N*-dimethylformamide (DMF) at 60°C. The solution was poured into excess methanol and the acetalized polymer was separated by filtration. It was further purified by reprecipitation from DMF solution into methanol and finally dried under vacuum at 80°C. 1.14 g of *p*-NAn-PVA was obtained. The other acetalized PVAs based on *p*-nitrobenzaldehyde (*p*-NBA), *m*-nitrobenzaldehyde (*m*-NBA), *N*-(2,4-dinitrophenyl)-aminoacetaldehyde dimethylacetal (DN) were also synthesized in the same way.

Preparation of Langmuir–Blogett (LB) Films.

50 mg of acetalized PVAs were dissolved in DMAc (15 ml) and diluted to 50 ml with benzene. (The concentration was about 0.1 wt%.) The solution was spread on water to form a thin film which was deposited onto glass substrate by means of the LB vertical lifting method using a Lauda film balance.

Electric Field Poling.

Acetalized PVAs were dissolved in DMF at about 10 wt% and were spincoated at 4000 rpm on a glass plate which had ITO electrode on the surface. The coating temperature was controlled at 60°C. The spincoated film was heated near T_g , and applied high voltages (5–10 kV) for 30 minutes. After cooling to 40°C, SHG was measured immediately. The film thickness was measured by ellipsometer or by tali-step method.

Second Harmonic Generation Measurement

Nd:YAG laser, with wavelength 1.064 μm ,

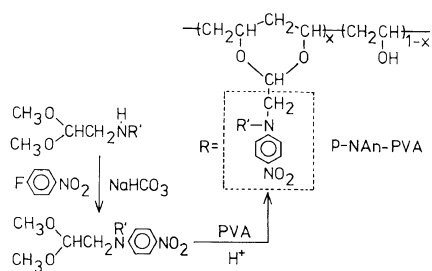


Figure 1. Synthetic route of acetalized PVA.

Q -switched, 10 mJ at a 10 Hz repetition rate, with a 500 μm diameter beam, was used to measure a light intensity at 0.532 μm as second-harmonic generation. The second-harmonic intensity of the films were measured using p - or s -polarized excitation and p - or s -detection.

RESULTS AND DISCUSSION

Synthesis of Acetalized PVA

The polymer of p -NAN-PVA was prepared by the acetal exchange reaction of N -(4-nitrophenyl)aminoacetaldehyde dimethylacetal with PVA in water using hydrochloric acid as a catalyst. The crude polymer was purified by reprecipitation method. (Figure 1) The introduction ratio (x) of the side chains (Table I) were calculated using the elemental analysis data. The obtained acetalized PVAs and analytical data are summarized in Table I.

Electric Field Poling

This process consisted of two steps. The first step was polymer coating on the substrate, and the second step was voltage application to the coated polymer.⁹ The synthesized acetalized PVAs were spin-coated on the glass substrate. The transparency of the spin-coated films depended on temperature. When spin-coated at 20–50°C microcrystals deposited on the substrate, which might be resulted from the rapid lowering of the substrate temperature. When spin-coated at 60–100°C, no microcrystals deposited and film was very transparent and uniform. The cut-off wave length of

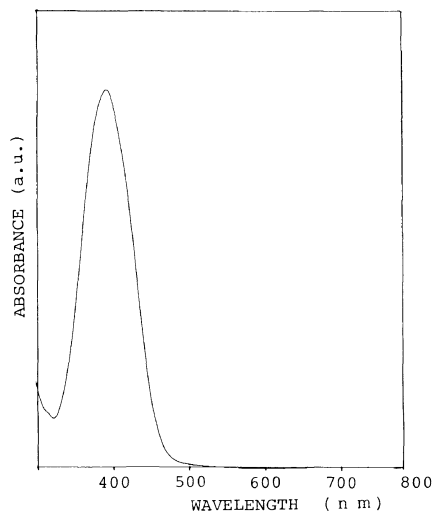


Figure 2. Absorption spectra of p -NAN-PVA film.

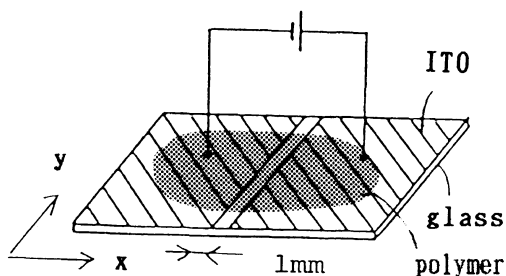


Figure 3. Electric field poling.

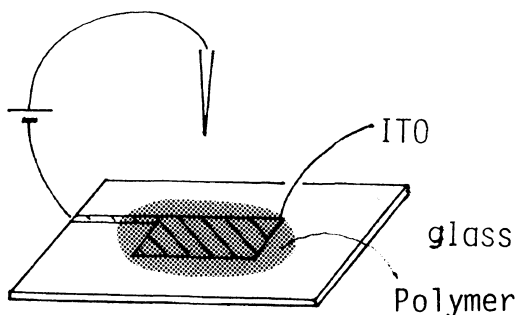


Figure 4. Corona electrical poling.

p -NAN-PVA film was 500 nm as shown in Figure 2. The coated polymer was amorphous and no scattering due to microcrystal took place. This means 0.532 μm SHG of Nd:

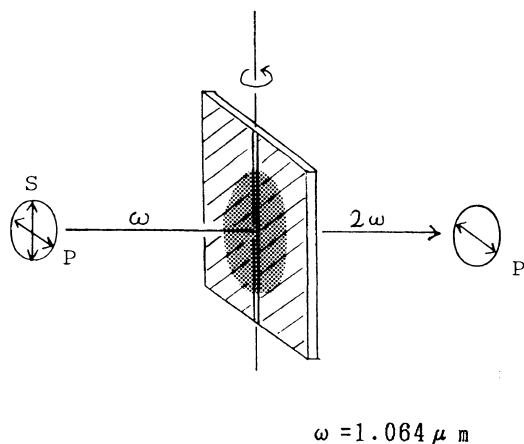


Figure 5. Measurement of SHG of poled polymer.

YAG laser can be emitted from the polymer without absorption. Tali-step technique and m-line wave guide technique were used for the measurement of the film thickness and refractive indexes. The coated film on the ITO electrode was heated near T_g , and cooled to room temperature under the electric field. Contact poling using slit type substrates as shown in Figure 3 and corona poling using plane type substrate as shown in Figure 4 were studied. The slit type was convenient for microscopic observation of the polymer orientation. The applied voltage was 2–3 kV and the slit width was 1 mm. However, insulation was broken down easily under the high electric field. On the other hand, in the case of corona poling, the spin-coated polymer film attached only one ITO surface and insulation was hardly broken down under the high electric field. The applied voltage was 6 kV and the film thickness was $0.25 \mu\text{m}$.

The SHG coefficient was measured with Marker-fringe method using Q-switched ND:YAG laser operating at $1.064 \mu\text{m}$ as illustrated in Figure 5. Figure 6 shows fringe pattern from *p*-NAn-PVA using slit type substrate. "ps" means S-polarized beam was introduced and P-polarized SHG was observed. "pp" beam was 7 times larger than "ps" beam. This implies that SHG was dependent on the

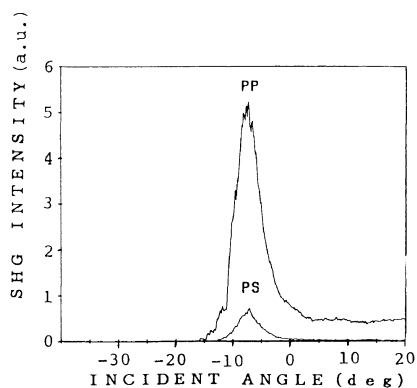


Figure 6. SHG of *p*-NAn-PVA (slit type substrate).

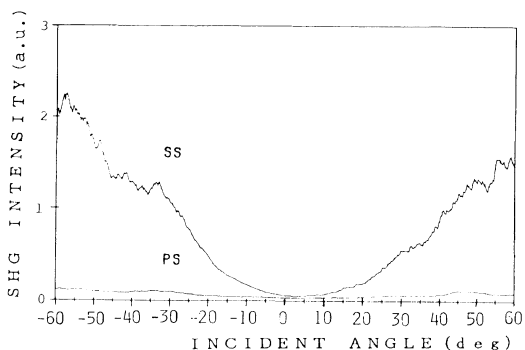


Figure 7. SHG of *p*-NAn-PVA (plane type substrate).

orientation of the side chains of the polymer. *p*-NAn-PVA and DN-PVA showed SHG, while *p*-NBA-PVA and *m*-NBA-PVA did not. Only *p*-nitro aniline structure of the side chain was effective for the SHG activity.

When the slit type substrate was used, the maximum SHG intensity was observed when the incident angle was 0° . This implies that the side chains oriented toward inplane electric field direction.

When corona poling was used, the maximum intensity was observed when the incident angle was more than 50° as shown in Figure 7. This means also that the side chains were oriented toward the electric field direction, that is, out of plane direction. The SHG activity of this corona poled film was estimated in comparison to quartz d^{11} -constant.¹⁰ The refractive

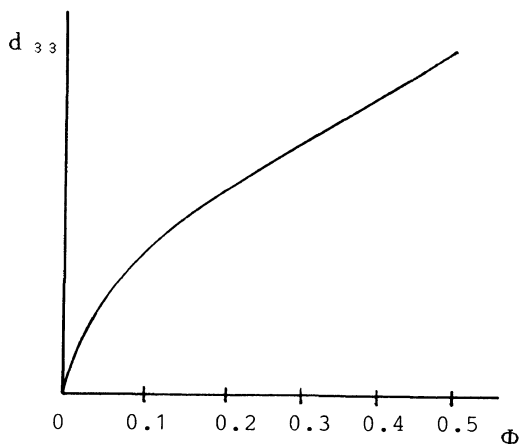


Figure 8. Calculated relationship between d_{33} and Φ .

indexes of *p*-NAn-PVA were measured using m-line method.¹¹ The *d*-constant of *p*-NAn-PVA was calculated by using $n_{\omega} = 1.587$ ($\omega = 1064$ nm) $n_{2\omega} = 1.690$ ($2\omega = 514$ nm). The calculated *d*-constant was 40.8 pm V^{-1} even 7 days after the poling.

The orientation and relaxation degree of corona poled films were determined from absorbance changes. The absorbance decreased once by poling,¹² and increased in the course of the relaxation. This was due to the out of plane orientation of the side chains. The order parameter of side chain poled film was determined using absorption measurements.

$$\Phi = 1 - A/A_0 \quad (1)$$

Where Φ is the order parameter, A is the absorbance of a poled film, A_0 is the absorbance of a unpoled polymer film.

The order parameter of electric field poled polymer can be described as eq. 2

$$\Phi = 1/2 * (3L_{2(p)} - 1) \quad (2)$$

$$p = \frac{\varepsilon(n^2 + 2)\mu'}{(n^2 + 2\varepsilon)} \frac{E}{kT} \quad (3)$$

where ε is the dielectric constant, n is the refractive index, μ is the dipole moment of the side-chain, E is the electric field at the side-chain, k is the Boltzmann constant, T

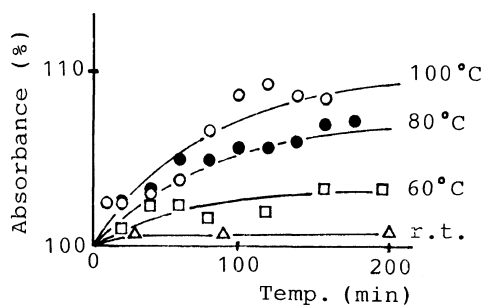


Figure 9. Absorption increasing curves at various temperatures.

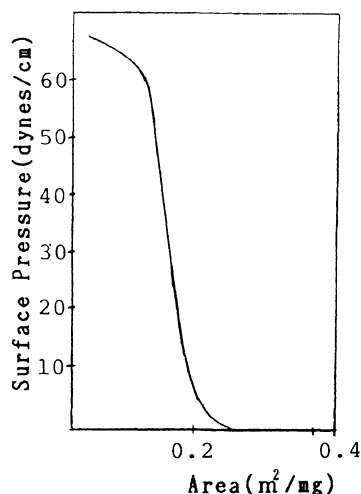


Figure 10. Surface pressure-area isotherm of *p*-NAn-PVA (20.1°C).


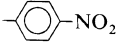

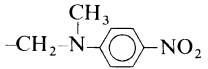
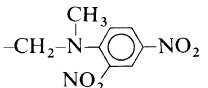
is the absolute temperature, and L_2 is the 2nd-order Langevin function.

The non-linear coefficient (d_{33}) can be described as eq. 4 if the internal electric fields produce only dipole orientation of the side chain.

$$d_{33} = Nf_{\omega}f_{\omega}f_{2\omega}L_{3(p)}\beta \quad (4)$$

where N is the side-chain density, f the local field factor, L_3 is the 3rd-order Langevin function, and β is the second-order polarizability tensor component of the side-chain. The subscript 2ω and ω refer to second-harmonic and fundamental radian frequencies, respectively. Since side-chain moiety that

Table I. Properties of acetalized PVAs

| | Side chain R | χ | T_g °C | T_d °C | Limiting area (Å ² /unit) | Addition ratio of OA-PVA | Up-lift deposition ratio ^b |
|---------------------|---|--------|-------------|-------------|---|--------------------------------|---|
| OA-PVA | -(CH ₂) ₆ -CH ₃ | 0.819 | 34.0 | 364.0 | 33.61 | — | — |
| BA-PVA ^a |  | 0.775 | 130 | 286 | 30 | — | — |
| <i>p</i> -NBA-PVA |  | 0.419 | 135.7 | 291.2 | — | 5 wt% | 0.62 |
| <i>m</i> -NBA-PVA |  | 0.506 | 98.2 | 296.6 | 11.47 | 15 wt% | 0.77 |
| <i>p</i> -NAN-PVA |  | 0.88 | 115.0 | 308.5 | 4.41 | 1 wt% | 0.85 |
| DN-PVA |  | 0.591 | 99.0 | 286.8 | 2.75 | 1 wt% | 0.71 |

^a Reported value.

^b Up-lift deposition ratio = $\frac{\text{deposition during up-lift process}}{\text{deposition during up-lift and down process}}$.

consists of electron-donor and acceptor pairs is attached to a planar extended π -electron system, it is reasonable to assume that the predominant microscopic second-order polarizability tensor component β is parallel to the molecular dipole moment μ . So d_{33} is described by using Φ . Figure 8 shows computer simulation of d_{33} vs. Φ . d_{33} is proportional to Φ in the practical range of 0.2–0.4, so the optimization of corona poling condition and relaxation can be estimated by UV absorption measurement without SHG measurement.

The relaxation of SHG at various temperatures were observed using by absorbance increase of polymer film.¹² Figure 9 shows absorption at 390 nm increases with increasing temperatures. The absorbance just after electric field poling treatment was estimated as 100%. The final absorbance value was 110% at various temperatures. Compared to the other NLO side chain type polymers,¹³ *p*-NAN-PVA showed small SHG relaxation and were useful as a new type SHG material. The small relaxation behavior of the SHG activity might

be due to either the hydrogen bonding through hydroxy groups or a cross-linking reaction at the acetal group during the poling.

LB Orientation

The limiting area calculated from the surface pressure–area isotherm of *p*-NAN-PVA, which is shown in Figure 10 was 4.41 Å²/unit. This value was extremely small compared to that of OA-PVA (33.61 Å²/unit) (see Table I). The aggregate structure of *p*-NAN-PVA might reduce the limiting area because the *p*-nitro aniline moiety had a large dipole moment to form aggregate structure easily.¹⁴

This *p*-NAN-PVA was tried to deposit on the glass substrate by a vertical lifting method, but the film was too hard to deposit. To improve these two problems, softening of the monolayer film was examined. In case of OA-PVA, the film on water was very soft and formed Y-type deposition on the glass. So *p*-NAN-PVA was mixed with OA-PVA. Only with a 1 wt% addition of OA-PVA, it could be deposited on the glass, only during the

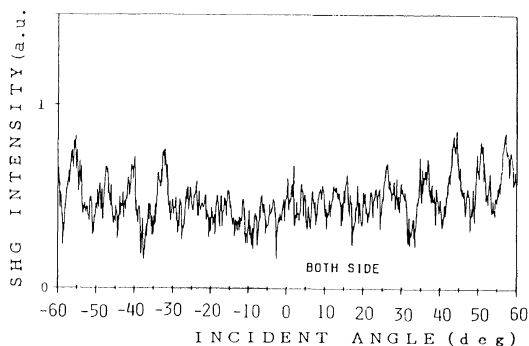


Figure 11. SHG of *p*-NAn-PVA (LB orientation).

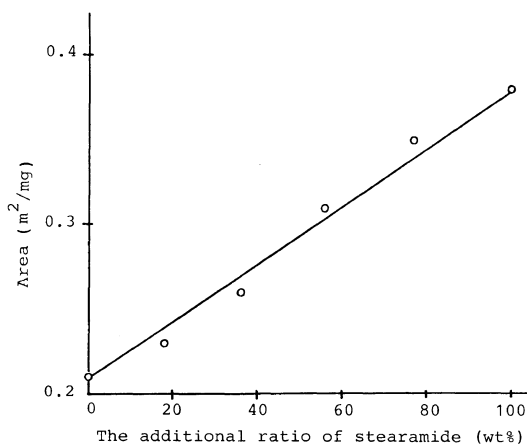


Figure 12. Limiting area of *p*-NAn-PVA mixed with stearamide.

up-lift process. Up-lift deposition ratio of the film is shown in Table I (footnote b). Table I shows obtained maximum value of up-lift deposition ratio. Only with 1 wt% addition of OA-PVA, *p*-NAn-PVA could make the best up-lift film. When more than 1 wt% of OA-PVA was added, then up-lift deposition ratio decreased. However this up-lift film showed no SHG activity. The aggregation of the *p*-NAn-PVA side chain may collapse monolayer film on water surface, and cancel the SHG activity of the polymer. OA-PVA acts as a softener but does not act as a support of the side chains.

Monomer type supports were examined

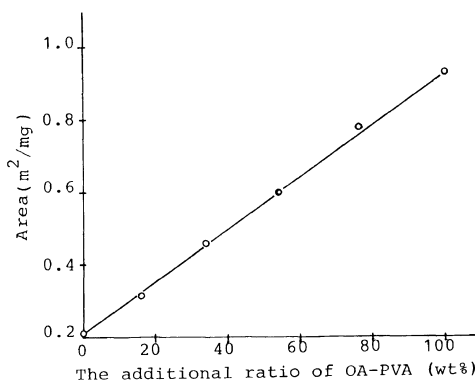


Figure 13. Limiting area of *p*-NAn-PVA mixed with OA-PVA.

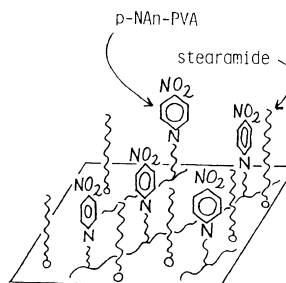


Figure 14. LB structure of *p*-NAn-PVA mixed with stearamide.

instead of OA-PVA. 33 wt% addition of stearamide gave an uniform LB-film on water, which was deposited on the glass only during the up-lift process. The up-lift deposition ratio was 1.31. This value (>1.00) was due to the small expansion of the film on water during the down process. The film was deposited on both side of the substrate by 14×2 layers. This sample gave SHG fringe pattern when the LB films were irradiated on both side of the substrate as shown in Figure 11, which implied vertical orientation of the side chains. However, the SHG activity of this LB-film could not be estimated because the observed SHG intensity was too weak. Figure 12 showed limiting area of *p*-NAn-PVA. When the additional ratio of stearamide was in the range of 10–50 wt%, the values of the

limiting areas were smaller than the calculated values of *p*-NAN-PVA. On the other hand, when OA-PVA was added to the *p*-NAN-PVA, the values of the limiting areas coincided with the calculated values of *p*-NAN-PVA as seen in Figure 13. This may mean that the stearamide filled the side chain space of polymer and made a fully-packed structure as shown in Figure 14. This fully-packed system may support *p*-nitroaniline side chains out of plane direction so as to make SHG active Z-type LB-film.

The role of the stearamide can be summarized as follows.

The Appropriate Softener of the Polymer.

When OA-PVA was used as a support, the film on water was too soft. More than 1 wt% addition of OA-PVA gave up-lift and down deposited film. On the other hand, stearamide as a support (0–33%) gave only up-lift deposited film. This may due to the structure of LB-film as illustrated in Figure 14. The stearamide may fill the side chain space of the polymer and would make fully-packed structure. This structure may not make the LB-film too soft, and gave up-lift film.

The Support of Side Chain of the Polymer.

The side chain of the pure *p*-NAN-PVA made aggregate structure due to the strong dipole moment of *p*-nitroaniline moiety of the side chain. The alkyl chains of stearamide may reduce the dipole moments and make vertical orientation of the side chains. This may help up-lift aggregated film to make Z-type oriented film, which was SHG active.

CONCLUSION

The *p*-NAN-PVA was synthesized, and two types of orientation methods, namely LB orientation and electric field poling were examined. SHG activity was observed by

both methods. Electric field poling was more effective than LB method. The poled film showed small relaxation of the SHG activity.

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REFERENCES

1. G. R. Meredith, J. G. Nandusen, and D. J. Williams, *Macromolecules*, **15**, 1385 (1982).
2. K. D. Singer, J. E. Sohn, and S. J. Lalama, *Appl. Phys. Lett.*, **49**, 248 (1986).
3. S. Matsumoto, K. Kubodera, T. Kurihara, and T. Kaino, *Appl. Phys. Lett.*, **51**, 1 (1987).
4. C. Ye, T. J. Marks, J. Yang, and G. K. Wang, *Macromolecules*, **20**, 2322 (1987).
5. K. D. Singer, M. G. Kuzyk, W. R. Holland, J. E. Sohn, S. T. Lalama, R. B. Comizzoli, H. E. Katz, and M. L. Schilling, *Appl. Phys. Lett.*, **53**, 1800 (1988).
6. M. Eich, B. Reck, D. Y. Yoon, C. Grant Willson, and G. C. Bjorklund, *J. Appl. Phys.*, **66**, 3241 (1989).
7. T. Senoh, K. Sanui, and N. Ogata, *Chem. Lett.*, 1849 (1990).
8. K. Oguchi, T. Yoden, Y. Kosaka, M. Watanabe, K. Sanui, and N. Ogata, *Thin Solid Films*, **161**, 305 (1988).
9. S. S. Barmji, K. J. Kao, and M. M. Perlamann, *J. Electrostat.*, **6**, 373 (1979).
10. J. Jerphagnon and S. K. Kurtz, *J. Appl. Phys.*, **41**, 1667 (1970).
11. G. Zhang and K. Sasaki, *Appl. Opt.*, **27**, 1358 (1988).
12. M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, and A. Dienes, *J. Opt. Soc. Am., B*, **6**, 733 (1989).
13. M. Eich, A. Sen, H. Looser, G. C. Bjorklund, J. D. Swalen, R. Twieg, and D. Y. Yoon, *J. Appl. Phys.*, **66**, 2559 (1989).
14. T. Inoue, K. Yase, M. Okada, S. Okada, H. Matsuda, H. Nakanishi, and M. Kato, *Jpn. J. Appl. Phys.*, **27**, 1635 (1988).