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# Second Harmonic Generation of Multilayer Films of Aromatic Polymers Formed by Langmuir-Blodgett Method

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Ultra-thin films of poly(benzothiazole) ($NO_2$-PBT) prepolymer which contained nitro groups were formed at air/water interface. Multilayer films of the $NO_2$-PBT prepolymer which were made by Langmuir-Blodgett (LB) technique showed second harmonic generation (SHG). The SH light intensity of the $NO_2$-PBT, however, which was obtained by heat treatment of the prepolymer was lower than that of the prepolymer.

Nonlinear optical (NLO) materials have potentially wide applications in the field of optical communications and data processing. Organic NLO materials are based on a single crystal and have problems of processability and thermal stability.[1,2] We have been studying the syntheses of aromatic polymer films, poly(benzimidazole) (PBI), poly(benzoxazole) (PBO), and poly(benzothiazole) (PBT) at air/water interface by LB method.[3-5] They are characteristic in terms of outstanding thermal and chemical stabilities. PBT is known to have an activity of third harmonic generation (THG) with irradiation of high energy laser beam because PBT is a fully conjugated polymer with donor groups.[6] In case of second harmonic generation (SHG), one needs a noncentrosymmetric and highly polar structure in which donor and acceptor groups are uniformly oriented. Therefore, incorporation of electron accepting group to PBT is required to the SHG activity. Poly(benzothiazole) ($NO_2$-PBT) which contained nitro groups as an acceptor to poly(benzothiazole) was designed. Ultra-thin films of the $NO_2$-PBT prepolymer and multilayer films were made by LB technique which would provide a good orientation of SHG active polymers. SHG of multilayer films of the $NO_2$-PBT prepolymer and the $NO_2$-PBT which was obtained by heat treatment were evaluated.

Figure 1 shows synthetic scheme of the ultra-thin film of the $NO_2$-PBT

prepolymer at air/water interface. 2-nitro-dihexylterephthalaldimine (1) was synthesized by refluxing nitroterephthalaldehyde, which was obtained by nitration reaction of terephthalaldehyde, with 2 moles of hexylamine in benzene at 80°C for 12 hours. 1 in benzene (0.1wt%) was spread dropwise onto aqueous solution of 2,5-diamino-1,4-benzenedithiol (2) (0.001wt%). Polymerization proceeded with standing the solution at room temperature. After 4-8 hours later, the ultra-thin film of the $NO_2$-PBT prepolymer was obtained on water surface.

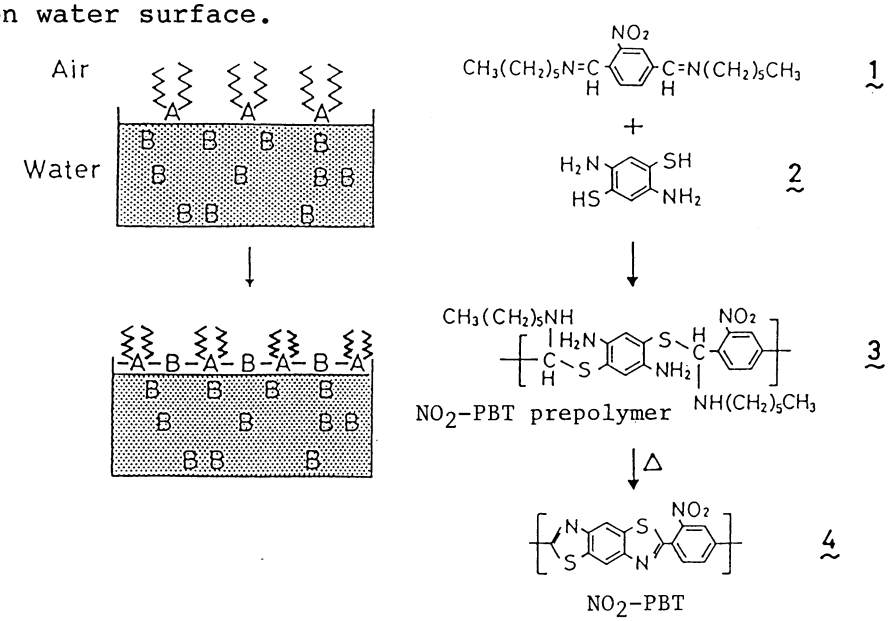


Fig.1. Synthetic scheme of the ultra-thin film at air/water interface.

The $NO_2$-PBT prepolymer film, however, could not be deposited onto a glass substrate by a vertical lifting method of LB technique by means of a conventional LB trough. This result was caused by friction between the film on water surface and the wall of the LB trough. Therefore, we modified the trough to a moving-wall type trough which had 'Teflon' seals, which could be moved with a pressure bar, along the walls of the trough to prevent friction. It was important to modify the surface of a glass substrate by previously depositing acetalized polyvinylalcohol because of increasing affinity between the surface of the substrate and the $NO_2$-PBT prepolymer film. Figure 2 shows the result of the deposition of the $NO_2$-PBT prepolymer film by the improved method by means of the moving-wall trough. The film was deposited and the deposition ratio was ca.1. The deposition was occured by only up-stroke, that is, Z-type deposition was attained. This result means that the multilayer film of the $NO_2$-PBT prepolymer has a noncentrosymmetric structure which is absolutely neccessary for SHG material.

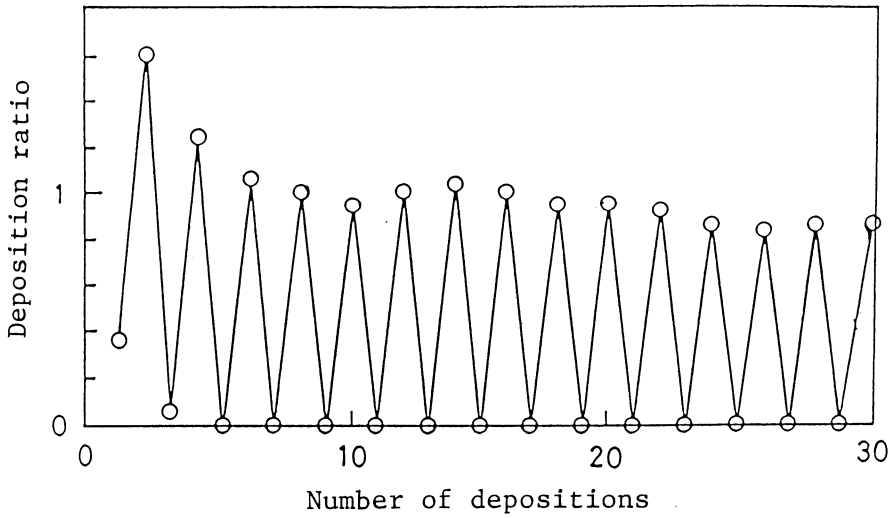


Fig.2. Result of the deposition of the $NO_2$-PBT prepolymer film with the improved method.

SHG of these multilayer films ranging from 2 to 40 layers on both sides in thickness was measured as follows. Nd:YAG laser beam (1064nm) was irradiated to a sample on a rotational stage, and the genarated second harmonic light (532nm) was detected by a photomultiplier after filtering off the remaining fundamental light. The multilayer films were irradiated with the laser beam perpendiclar to the layer plane.

Figure 3 shows a result of SHG measurement of the $NO_2$-PBT prepolymer multilayer film (20 layers). Fringe pattern of SH light intensity, which depended on the incidence angle of laser beam, was observed. This result suggests that the multilayer film of the $NO_2$-PBT prepolymer has the orientation of its molecular chain out of the surface of the substrate with a constant angle.

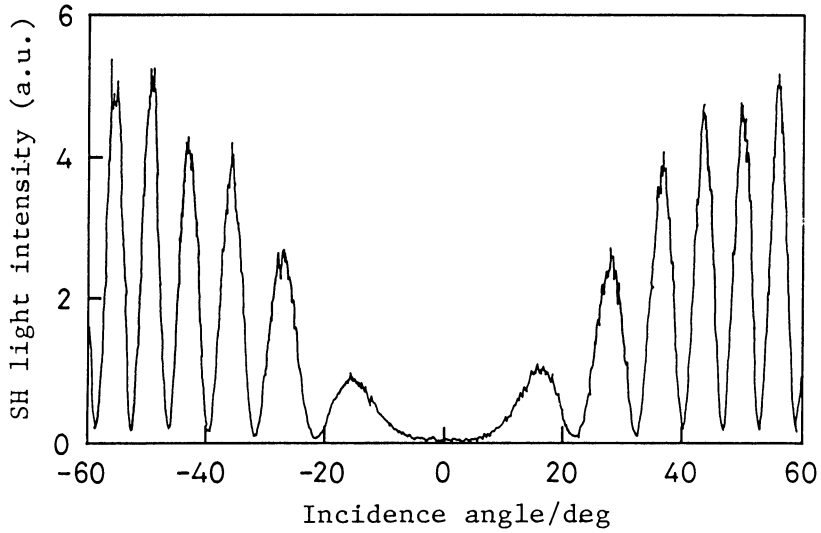


Fig.3. Fringe of SHG produced by the multilayer film of the $NO_2$-PBT prepolymer.

The SH light intensity is given by Eq. 1:[7]

$$I^{2\omega} = \frac{2\omega^2 d_{eff}^2 l^2}{c^3 \varepsilon_0 (n^{\omega})^2 (n^{2\omega})} (I^{\omega})^2 \operatorname{sinc}^2 \left(\frac{\Delta k l}{2}\right) \quad (1)$$

where sincX denotes (sinX)/X, $l$ is the sample thickness, $d_{eff}$ is the effective nonlinear optical susceptibility, n is the refractive index, c is the speed of light, and $k=k_2-2k_1$ is the phase mismatch between the fundamental and the SH waves with wave vectors $k_1$ and $k_2$, respectively. In agreement with theory (Eq. 1) the measured SH light intensity increased quadratically with the number of layers, that is, the thickness of multilayer films. It was concluded that the observed SH light was produced by the multilayer films of the $NO_2$-PBT prepolymer.

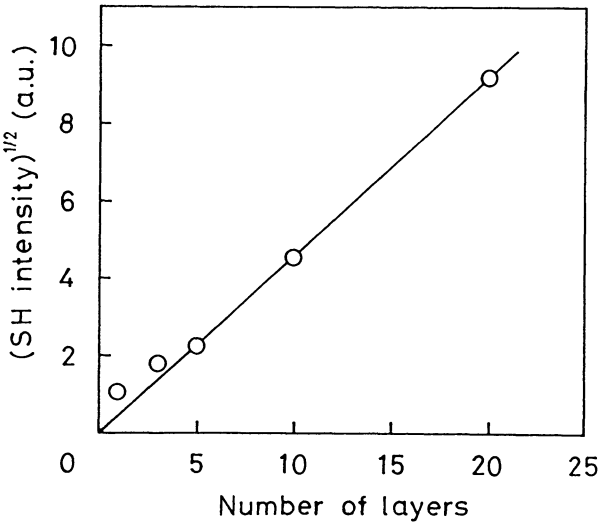


Fig.4. Square root of the SH intensity as a function of the number of layers.

The multilayer films of the $NO_2$-PBT were obtained by heat treatment of prepolymer films at 300°C. The result of the SHG measurement of these films showed fringe patterns of SH light intensity, but the intensity of the $NO_2$-PBT decreased to one fortyth of the prepolymer. It was presumed that the decrease of the SH light intensity was caused by the alteration of the molecular structure and the disorder of layers by heat treatment.

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References

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