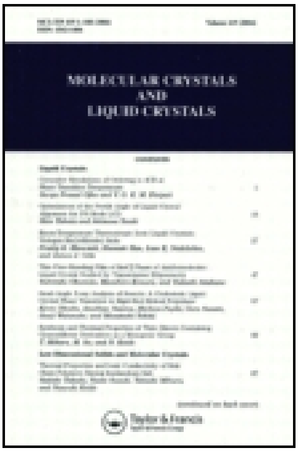

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OPTICAL THIRD-HARMONIC GENERATION IN POLY(*p*-PHENYLENE BENZOBISTHIAZOLE) LANGMUIR-BLODGETT FILM

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Abstract The nonlinear optical anisotropy of poly(*p*-phenylene benzo-bisthiazole) (PBT) Langmuir-Blodgett (LB) films has been investigated by optical third-harmonic generation measurement. Polymer backbones of PBT in LB films were aligned along the dipping direction. The $\chi^{(3)}_{xxxx}$, $\chi^{(3)}_{yyyy}$ and $\chi^{(3)}_{xxyy}$ values were determined by rotational Maker fringe method to be 11.3×10^{-12} esu., 1.5×10^{-12} esu. and 0.9×10^{-12} esu, respectively. These nonlinear optical anisotropies can be explained well by assuming a Gaussian orientational distribution of one-dimensional π-conjugated chains.

INTRODUCTION

Poly(*p*-phenylene benzobisthiazole) (PBT) is one of the well-studied π-conjugated heterocyclic rigid-rod polymers and has received a strong attention due to its inherently superior physical and chemical properties such as mechanical strength, thermal stability and solvent resistance.[1] Previous nonlinear optical (NLO) studies show that PBT exhibits a large third-order and ultrafast NLO responses.[2,3] However, its poor processability, i.e., insolubility in organic solvents, makes it difficult to obtain thin films with good optical quality for the detailed and accurate NLO studies.

Langmuir-Blodgett (LB) technique offers a unique approach to fabricate uniform, good optical quality multilayer film with improved molecule packing. The Y-type LB film tends to form an in-plane anisotropy coming from the preferential alignment of the long chain molecules along the dipping direction.[4,5] Recently, Kakimoto *et al.* developed highly oriented PBT LB films through precursor route.[6] In this paper, we present third-order nonlinear susceptibility measurements by optical third-harmonic generation (THG) in the PBT LB films, and discuss the degree of alignment of polymer chains assuming the Gaussian orientational distribution of one-dimensional π-conjugated systems.

EXPERIMENTAL

The chemical structure of PBT used in this study is shown in Figure 1. The PBT LB films were prepared through their precursor films. The precursor polymers consist of a long-chain alkyl amine salts, and the polyamides derived from 2,5-di(carboxyethylthio)-1,4-phenylenediamine and aromatic dicarboxylic acid chlorides. Y-type multilayers were deposited on a fused silica substrate with a surface pressure of 40 mN/m. The film was subsequently heated at 280°C for several hours to convert to the PBT LB film. The detailed fabrication of the PBT LB films will be reported separately.[6]

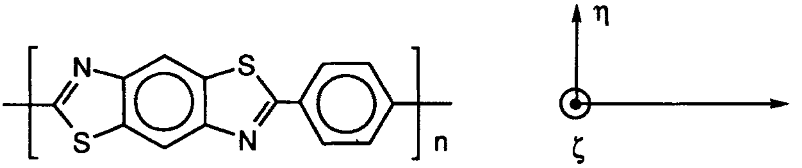

FIGURE 1 Chemical structure of PBT and molecular coordinate.

The evaluation of anisotropy properties of the PBT LB films was carried out by THG measurement at a wavelength of 1907nm as a function of the orientational angle φ. The angle φ was defined as the angle of dipping direction with respect to the polarization of the incident light. The details of the THG measurement set-up have been reported elsewhere.[7] In the measurement, the incident fundamental light was *s*-polarized and the *s*-polarized third-harmonic signals were detected. The fused silica plate was used as a reference ($\chi^{(3)}_{\text{fused silica}}=1.4 \times 10^{-14}$ esu).

RESULTS AND DISCUSSION

Figure 2 shows absorption spectrum of PBT LB film measured with non-polarized light. There are no absorption in both fundamental and third-harmonic wavelengths. Therefore the $\chi^{(3)}$ values obtained in this study are off-resonant ones. The dependence of $\chi^{(3)}$ on the angle between the average chain direction and the polarization of fundamental light is shown in Figure 3. Under this experimental arrangement, the third-order optical susceptibility tensor $\chi'^{(3)}$ in the laboratory framework [(X,Y,Z) with X axis along the polarization direction of the light] is related to $\chi^{(3)}$ components in the film based framework [(x,y,x) with x axis along the dipping direction] as follows:

$$\chi'^{(3)}_{XXXX} = \chi^{(3)}_{xxxx}\cos^4\varphi + \chi^{(3)}_{yyyy}\sin^4\varphi + 6\chi^{(3)}_{xxyy}\sin^2\varphi\cos^2\varphi. \qquad (1)$$

The experimental data were fitted to Eq.(1) as shown in Figure 3. The analysis shows that the components are

$$\begin{aligned} &\chi^{(3)}_{xxxx} = 11.3\times10^{-12}\mathit{esu}, \\ &\chi^{(3)}_{yyyy} = 1.5\times10^{-12}\mathit{esu}, \qquad (2) \\ \text{and} \quad &\chi^{(3)}_{xxyy} = 0.9\times10^{-12}\mathit{esu}. \end{aligned}$$

The in-plane anisotropy of this Y-type LB film has been attributed to the preferential alignment of molecules along the dipping direction. The shear force coming from the hydrophilic or hydrophobic affinity between the stacked monolayers on the substrate and the floating monolayer at the subphase surface in the film transfer process makes the polymer chains aligned along the dipping direction. This brings macroscopically a large anisotropy and dense molecular packing in the transferred films.

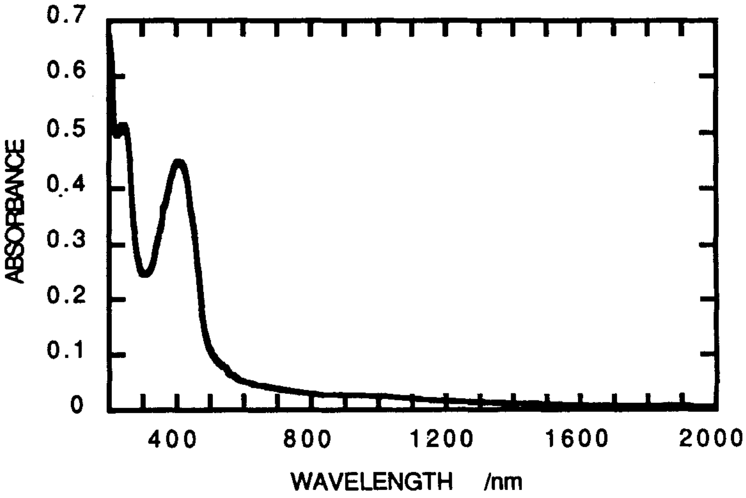

FIGURE 2 The absorption spectrum of the PBT LB film.

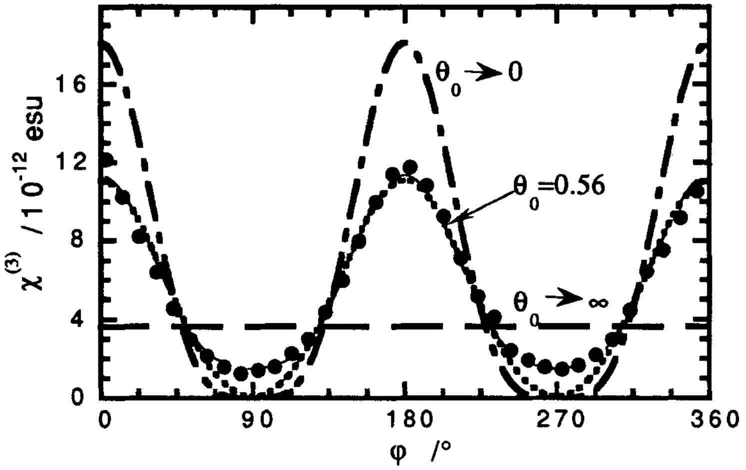

FIGURE 3 $\chi^{(3)}$ values measured at different angles φ between the dipping direction and the polarization of the light. The solid circles represent the measured data. The solid curve is the theoretical fitting according to Eq.(1). The dotted curve is the theoretical fitting under the assumption of Gaussian orientational distribution function (θ_0=0.56). The dash-dotted line and the broken line are $\chi^{(3)}$ assuming a perfect alignment ($\theta_0 \to 0$) and random distribution ($\theta_0 \to \infty$), respectively.

In a linearly conjugated polymer, the π-electrons at the ground state are delocalized along the chain direction, i.e., ξ-direction as shown in Figure 1. In case of PBT, the conjugation length in the chain transverse direction is about the dimension of a benzene ring, which is much shorter than that along the polymer chain. The macroscopic third-order susceptibility $\chi^{(3)}_{ijkl}$ relates to the microscopic second hyperpolarizability γ, in general, by the following equation:[8]

$$\chi^{(3)}_{ijkl} = N\left\langle R_{ii'}R_{jj'}R_{kk'}R_{ll'}\gamma^{*}_{i'j'k'l'}\right\rangle$$

$$= \frac{N\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\psi F(\phi,\theta,\psi) R_{ii'}R_{jj'}R_{kk'}R_{ll'}\gamma^{*}_{i'j'k'l'}}{\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\psi F(\phi,\theta,\psi)}, \qquad (3)$$

where $\gamma^{*}_{i'j'k'l'} = \gamma^{3\omega}_{i'i'}\gamma_{i'j'k'l'}f^{\omega}_{j'j'}f^{\omega}_{k'k'}f^{\omega}_{l'l'}$, f's are components of the local-field correction tensor for anisotropic media, N is a number of molecules per unit volume, R's are the rotation matrices transforming the molecular frame to the film based frame, $F(\phi,\theta,\psi)$ is the orientational distribution function at the Euler angle ϕ, θ and ψ.

The evaluation of the orientational distribution function of molecules requires to deduce the molecular polarizabilities from observed macroscopic susceptibilities. We used the simple assumption that the orientational distribution of polymer chains follows a Gaussian function,

$$F(\phi,\theta,\psi)=\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right], \tag{4}$$

where θ is an angle of the individual polymer chain with respect to the dipping direction as defined by Eular angle. The parameter θ_0 is related to the standard deviation as $\sigma=\theta_0/\sqrt{2}$. $\theta_0\rightarrow 0$ means a perfect uniaxial alignment of the chains, while $\theta_0\rightarrow\infty$ a random distribution of the chains. Under this assumption, expressions of the components of third-order optical susceptibility tensor $\chi^{(3)}$ were derived from Eq.(3) as

$$\chi^{(3)}_{xxxx}=N\gamma^*_{\xi\xi\xi\xi}\frac{\int_0^\pi d\theta\sin\theta\cos^4\theta\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right]}{\int_0^\pi d\theta\sin\theta\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right]},$$

$$\chi^{(3)}_{yyyy}=\frac{3}{8}N\gamma^*_{\xi\xi\xi\xi}\frac{\int_0^\pi d\theta\sin^5\theta\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right]}{\int_0^\pi d\theta\sin\theta\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right]},$$

$$\chi^{(3)}_{xyyx}=\chi^{(3)}_{xyxy}=\chi^{(3)}_{xxyy}=\chi^{(3)}_{yyxx}=\chi^{(3)}_{yxyx}=\chi^{(3)}_{yxxy}$$
$$=\frac{1}{2}N\gamma^*_{\xi\xi\xi\xi}\frac{\int_0^\pi d\theta\sin^3\theta\cos^2\theta\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right]}{\int_0^\pi d\theta\sin\theta\exp\left[-\left(\frac{\theta}{\theta_0}\right)^2\right]},$$

$$\chi^{(3)}_{xyxx}=\chi^{(3)}_{xxyx}=\chi^{(3)}_{xxxy}=\chi^{(3)}_{xyyy}=\chi^{(3)}_{yxxx}=\chi^{(3)}_{yyyx}=\chi^{(3)}_{yyxy}=\chi^{(3)}_{yxyy}=0. \tag{5}$$

The measured data were fitted again by using Eq.(1) and Eq.(5) with θ_0 and $N\gamma^*_{\xi\xi\xi\xi}$ as adjustable parameters. The orientational angle dependence of $\chi^{(3)}$ values was well fitted with θ_0=0.56 as shown by the dotted curve in Figure 3. One of the reasons why the experimental data around 90° and 270° are larger than the theoretical prediction in which a perfect one-dimensional molecular chain was assumed may be considered as $\gamma^*_{\xi\xi\xi\xi}$ is the only non-zero component of second-order polarizability tensor in the molecule based framework. In fact, another component also contributes to $\chi^{(3)}$, and these contributions become more significant when the polarization of the fundamental beam is perpendicular to the dipping direction (90° and 270°), where the contribution from $\gamma^*_{\xi\xi\xi\xi}$ is minimum.

The value of $N\gamma^*_{\xi\xi\xi\xi}$ corresponds to the maximum $\chi^{(3)}$ that is accessible if the polymer chains are perfectly aligned. The $\chi^{(3)}$ value for a random molecular distribution is only one fifth of $N\gamma^*_{\xi\xi\xi\xi}$ value. Figure 3 also shows the effect of polymer alignment degree (parameter θ_0) on the $\chi^{(3)}$ value. For a perfect alignment ($\theta_0 \rightarrow 0$), the maximum $\chi^{(3)}$ reaches 18.1×10^{-12} esu, while for a random distribution ($\theta_0 \rightarrow \infty$), $\chi^{(3)}$ is only about 3.6×10^{-12} esu. The molecular alignment of the sample investigated (θ_0=0.56) was compared with the two extreme situations.

CONCLUSION

THG measurements were performed on PBT LB film. The $\chi^{(3)}$ values were evaluated as a function of orientational angle. The $\chi^{(3)}$ values of the LB film are $\chi^{(3)}_{xxxx} = 11.3 \times 10^{-12}$ esu and $\chi^{(3)}_{yyyy} = 3.5 \times 10^{-12}$ esu. These anisotropies can be explained well by a Gaussian distribution function of the PBT polymer chains with the standard deviation $\sigma = 0.40$.

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