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Orientational dynamics in the crystalline and amorphous states of side-chain liquid crystalline polysiloxane probed by second harmonic generation

Makoto Hasegawa[a], Nobukatsu Nemoto[b], Yu Nagase[b], Yasuo Shirai[c], Tomiki Ikeda[a,*], Jiro Abe[c]

[a]*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan*
[b]*Sagami Chemical Research Center, 4-4-1 Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan*
[c]*Department of Photo-optical Engineering, Faculty of Engineering, Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi, Kanagawa 243-02, Japan*

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Abstract

The orientational behaviour of mesogenic chromophores in side-chain liquid crystalline polysiloxane subject to an external electric field was investigated by the measurement of second harmonic generation (SHG). The rise and decay rates of the electric-field-induced SHG intensity in the crystalline state were found to be slower than those in the amorphous state; furthermore, the SHG intensity in the crystalline state was found to be weaker than that in the amorphous state. Analysis of the rise and decay rates of the electric-field-induced SHG intensity suggested that the mesogenic chromophores in the amorphous state move independently with other mesogenic chromophores and with the siloxane backbone, whereas those in the crystalline state move cooperatively with them.

Keywords: Side-chain liquid crystalline polysiloxane; Second harmonic generation; Nonlinear optical materials

1. Introduction

It has been well established that molecules containing an electron donor and acceptor, attached to a π-conjugated system, have a strong permanent dipole moment and present large first-order hyperpolarizabilities. However, groups with a strong permanent dipole moment tend to form antiparallel conformations in a condensed phase, and this gives rise to centrosymmetry in the materials and diminishes the second-order nonlinear susceptibility, $\chi^{(2)}$, of the materials [1–3]. Random arrangement of the second-order NLO chromophores doped or covalently linked to polymers also decreases $\chi^{(2)}$ in spite of the large microscopic optical nonlinearity of the NLO chromophores. In order to obtain amorphous second-order NLO polymers with large $\chi^{(2)}$ values, it is necessary to induce noncentrosymmetry in the polymeric system by applying an external electric field [4]. However, this electric-field-induced second-order nonlinearity will gradually decrease after removal of the electric field. In corona poling, the dynamics of the charge deposition, the charge decay, and the orientational dynamics of the NLO chromophores are known to affect the time dependence of the SHG signal. The behaviour of this relaxation of the NLO chromophores has been investigated with the measurement of second harmonic generation (SHG) [5–19]. The measurement of the SHG intensity to monitor the relaxation can be of general utility in understanding the nature of dynamics in the solid state polymer. SHG is ideally suited for observing the motional dynamics associated with the relaxation of anisotropic order, since the SHG intensity is highly sensitive to orientational order of NLO chromophores. Thus, detailed information about the polymer conformation and mobility can be obtained from the analysis of the relaxation processes of the SHG intensity after removal of an external electric field.

In our previous papers, the behaviour of the electric-field-induced dipolar alignment of mesogenic chromophores in thin films of side-chain liquid crystalline polysiloxane containing mesogenic NLO-active azo chromophores was presented [20,21]. The polymer exhibits a smectic C liquid crystalline phase in the range 59–113°C, and the glass transition point is observed near −19°C. Moreover, the polymer shows two different kinds of solid state, i.e. amorphous and crystalline states. The crystalline state can be easily obtained by heating the as-cast film to the mesophase temperature and cooling it to room temperature. It differs

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* Corresponding author.

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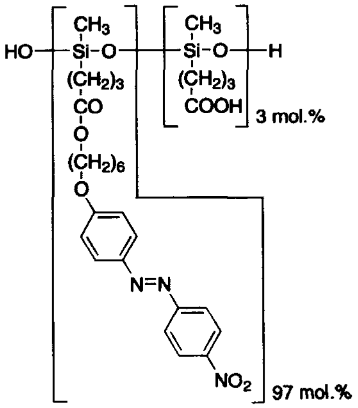

Fig. 1. Structure of polymer **1**.

from the amorphous state in the alignment of the mesogenic chromophores. It is found from spectroscopic investigations that the mesogenic chromophores in the crystalline state are aligned nearly normal to the substrate's surface and holds a layer structure formed in the mesophase. On the other hand, the mesogenic chromophores in the amorphous state are randomly aligned. Furthermore, the measurement of the temperature dependence of the electric-field-induced SHG intensity has suggested that the mesogenic chromophores form an antiparallel conformation in the crystalline state. Although the orientational relaxation behaviour of the NLO chromophores doped in amorphous polymers has been reported, the comparison of the orientational behaviour of the mesogenic chromophores between amorphous and crystalline states has not been made. In the present paper, the orientational behaviour of the mesogenic chromophores subject to an external electric field and the relaxation process after removal of the electric field in both the amorphous and crystalline states are investigated by analyzing the result of *in situ* SHG measurements.

2. Experimental

The side-chain functionalized polysiloxane (polymer **1**, Fig. 1) was prepared by the esterification of poly[(3-chlorocarbonylpropyl)methylsiloxane] with 4-{[4-(6-hydroxyhexyloxy)phenyl]azo}nitrobenzene. The introduction ratio of chromophores into the side chain of polysiloxane was 97 mol% ($M_n = 2.43 \times 10^3$, $M_w/M_n = 1.75$). Polymer **1** exhibits liquid crystallinity, as deduced from DSC measurements, polarized microscopic observation, and X-ray diffraction measurements. This polymer exhibits a smectic C phase in the range 59–113°C, and the glass transition was observed at − 19°C. Details of preparation and the results of those measurements have been published elsewhere [20,21]. Polymer films were prepared by spin coating from a THF solution with a concentration of 5 wt% of polymer **1**. The solution was first passed through a 0.50 μm Millipore filter to remove particulate impurities. An optically transparent thin film (1 μm thick) was prepared on a polyimide-coated ITO glass (EHC Co. Ltd) by spinning at 2000 rpm. The solvent-free film was obtained in a vacuum oven at 30°C for over 24 h.

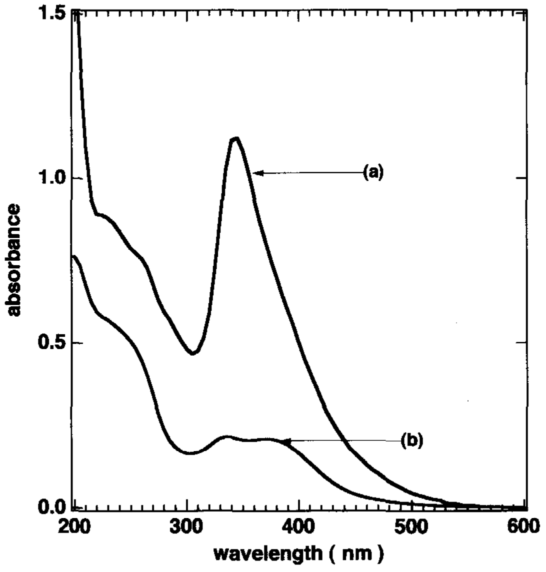

Fig. 2. UV–visible absorption spectra of the thin film in (a) the amorphous and (b) the crystalline states.

The corona discharge method was used to pole the sample by applying a negative voltage of 1.8 kV to a sharp tungsten needle located 5 mm in front of the grounded electrode onto which the polymer film was coated. The setup for the SHG measurement was identical to that used in previous work [20]. Basically, it consisted of a Q-switched Nd^{3+}:YAG laser operated at 10 Hz. The laser beam, the power of which was controlled by neutral-density filters, was directed through a $\lambda/4$ wave plate and a plate polarizer to convert it to a p-polarized beam. The sample holder was placed on a rotating stage and rotated around the horizontal axis. A p-polarized laser beam first passing through a UV–visible light cutoff filter was focused on the sample film. An infrared-absorbing filter, an analyzer and an interference filter were used following the sample to detect only the p-polarized SH signal with a PM tube. The SH signal detected by the PM tube was processed with a boxcar integrator which was interfaced to a personal computer. The film sample was fixed at an incidence angle of 50°.

3. Results and discussion

3.1. *Conformational characterization of the thin films*

The crystalline state thin film can be easily obtained by heating the as-cast amorphous film to the mesophase temperature and cooling it to room temperature. Fig. 2 shows the UV–visible absorption spectra, which were measured by a transmission method, for both the crystalline and amorphous states obtained from an identical thin film sample. It should be noted that one can find a large

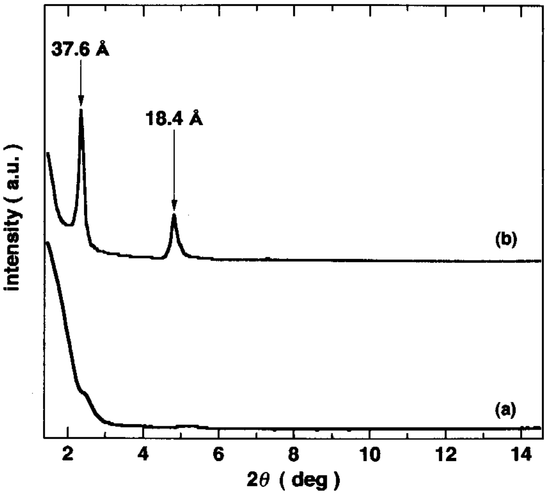

Fig. 3. X-ray diffraction patterns of the thin film in (a) the amorphous and (b) the crystalline states obtained by a thin film method.

difference in the intensity of the absorption band located around 370 nm between the two states. The absorption band at 370 nm is assigned to the $\pi-\pi^*$ electronic transition band of 4-nitro-substituted azobenzene chromophores, and the electric dipole transition moment is oriented nearly along the molecular long axis [22]. That is, the $\pi-\pi^*$ transition of the azo dye chromophore is polarized along the molecular long axis. When the electric vector of the light is parallel to the direction of the molecular long axis, the molecule absorbs light intensely. Considering the direction of the electric vector of light, the difference in the absorption band between the two states indicates the difference in the orientational direction of the mesogenic chromophores with respect to the surface of the substrate. In the amorphous state, the mesogenic chromophores are aligned randomly, whereas they are aligned nearly perpendicular to the substrate's surface in the crystalline state. The orientational behaviour of the mesogenic chromophores with phase transitions was reported in a previous paper [21].

X-ray diffraction patterns for the thin films in the two states measured by using a thin film method are shown in Fig. 3. Two sharp peaks were observed in the diffraction pattern of the thin film of the crystalline state, whereas no diffraction peaks were observed in that of the amorphous state. These results clearly indicate the formation of a periodical structure perpendicular to the substrate in the crystalline state. As described above, this polymer exhibits a smectic C phase and the layer structure which was formed in the temperature range of mesophase could be held even in the crystalline state. Thus, a diffraction peak observed in the small-angle region at about 2.4° can be assigned to the layer spacing of 37.6 Å. Moreover, a diffraction peak observed in the small-angle region at about 4.8° can be assigned to the second-order reflection peak of the first peak. We also measured a diffraction pattern in the crystalline state by using a powder method and detected a strong sharp peak corresponding to 3.54 Å, in addition to the peaks observed by using the thin film method. This new peak can be tentatively assigned to the π-stacking between the azobenzene moieties. Considering the fact that no diffraction peaks resulting from the π-stacking were observed in the diffraction pattern in the crystalline state measured by the thin film method, it is confirmed that the mesogenic chromophores are aligned perpendicular to the substrate's surface. As described in previous studies, the measurement of the SHG intensity shows that the mesogenic chromophores of the polymer form an antiparallel conformation with a layer structure in the crystalline states [20,21]. Such an antiparallel conformation of the mesogenic chromophores is electrostatically stable, since the mesogenic chromophores of this polymer have strong permanent dipole moments. Furthermore, it is considered that the mesogenic chromophores are packed with high density due to the π-stacking formed between the neighbouring azobenzene moieties. Possible conformations of the mesogenic chromophores in the two states derived from the above experimental results are illustrated in Fig. 4.

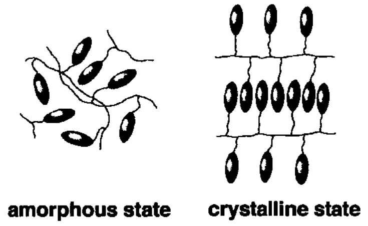

Fig. 4. Schematic drawings for the dipolar alignment of the mesogenic chromophores in the amorphous and the crystalline states.

3.2. Behaviour of the electric-field-induced SHG

In order to investigate the behaviour of the mesogenic chromophores subject to an external electric field, we have measured the electric-field-induced SHG intensity of

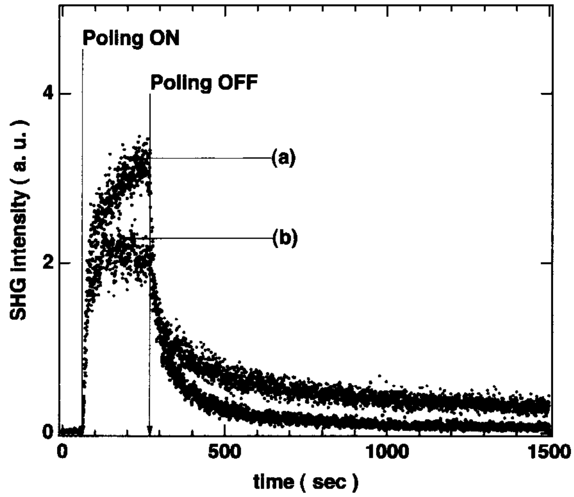

Fig. 5. Dependence of the SHG intensity in (a) the amorphous and (b) the crystalline states on application of the external electric field.

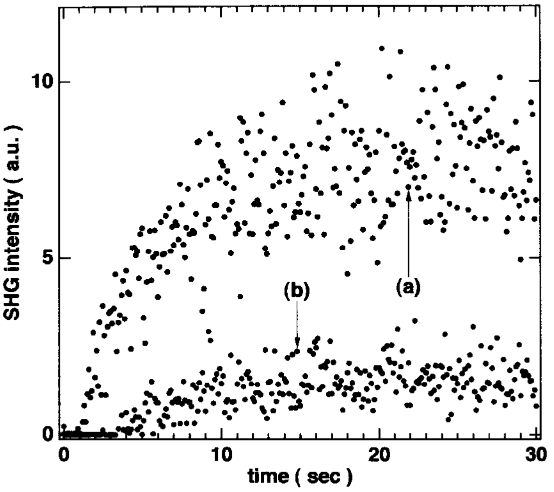

Fig. 6. Rise of the SHG intensity in (a) the amorphous and (b) the crystalline states.

the thin films in both the crystalline and amorphous states at room temperature, as shown in Fig. 5. The SHG signal was not observed before applying the electric field in these two states, indicating the negligibly small value of $\chi^{(2)}$ in these two states. The isotropic alignment of the mesogenic chromophores in the amorphous state makes the $\chi^{(2)}$ value small, whereas the mesogenic chromophores form an antiparallel conformation with a layer structure in the crystalline state and this gives centrosymmetric centres in the polymer film, also making the second-order optical nonlinearity vanish. When the sample was poled by the corona discharge method, the SHG intensity increased rapidly due to the destruction of centrosymmetry as a result of the chromophores' polar orientation. Immediately after the application of the electric field, the SHG intensity in the crystalline state rapidly saturates in contrast to that in the amorphous state. This result is significant, considering the difference in the response to an external electric field of the mesogenic chromophores between these two states. That is, the mesogenic chromophores in the amorphous state would be gradually aligned in the same direction. On the other hand, in the crystalline state, the alignment of the mesogenic chromophores in the same direction by overcoming the strong intermolecular interaction owing to the π-stacking between azobenzene moieties is considered to be difficult. Thus the appearance of the electric-field-induced SHG in the crystalline state is mainly considered to be attributable to the destruction of the centrosymmetric centres. Taking into account the rapid saturation of the SHG intensity in the crystalline state, it is suggested that the limitation of the displacement of the mesogenic chromophores would be present due to the molecular packing with high density. Further details of these mechanisms will be discussed in the next section. After removal of the electric field, both the SHG intensities in the crystalline and amorphous states decreased quickly. This rapid decay of the SHG intensity indicates that the orientational relaxation of the mesogenic chromophores takes place instantly. This rapid relaxation is considered to originate in the flexibility of the polysiloxane backbone as can be speculated from the low T_g of this polymer.

3.3. Induction process in the orientation of chromophores

In order to investigate the difference in the orientational behaviour subject to the electric field between the crystalline and amorphous states, we have carefully analyzed the growth processes of the electric-field-induced SHG signal as shown in Fig. 6. In this experiment, the averaging of the signal from the PM tube with the boxcar integrator was not performed. Furthermore, the corona discharge voltage was decreased to 1.6 kV in order to follow the effect of the electric field formation process inside the films on the electric-field-induced SHG. In the corona discharge method, an electric field inside a sample film is generated by the accumulation of negative charges on the surface. That is, an electric field formed inside a sample film will be gradually strengthened with time. Moreno and Gross also indicated that a certain period of time is required to allow the surface charge density to build up in the corona poling process [23]. The corona discharge was applied between 0 and 30 s in this experiment. As can be seen from Fig. 6, the SHG intensities in the two states did not grow immediately after applying the corona discharge. The growth rate of the SHG intensity in the crystalline state was slower than that in the amorphous one. It should be noted that the SHG intensity could not be observed until about 4 s after the application of the corona discharge in the crystalline state, while the SHG intensity began to grow only 1 s later after the application of the corona discharge in the amorphous state. This means that an electric field greater than a certain threshold is necessary for the destruction of the centrosymmetric centres in the crystalline state. Wang et al. compared the growth rate of the SHG intensity between the side-chain NLO polymer and the NLO-dye doped polymer, and they found that the SHG signals for the NLO-dye doped polymer reached their stable levels soon after an initial rapid growth [18]. Based on the experimental observations, they concluded that this rapid response was attributable to the effective decoupling of the motion of the NLO-dye chromophores from polymer segmental motion, and the electric-field-induced alignment of chromophores depends on both the size of the local free volume around each chromophore and the degree of the decoupling between the chromophore and the polymer backbone. The significance of our study lies in a different point of view. We have compared the orientational dynamics between the crystalline and amorphous states for the identical polymer. Although the coupling of the motion of the mesogenic chromophores with polymer segmental motion is an important factor in analyzing the dynamics, a crystal field effect, which has never been discussed in the poling dynamics of the side-chain NLO polymers, should also be taken into consideration.

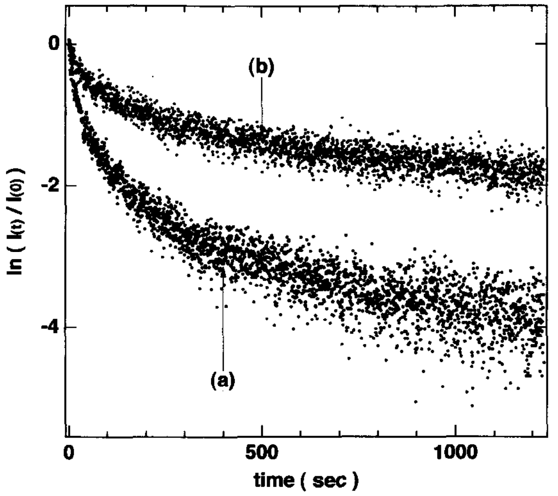

Fig. 7. Decay of the SHG intensity in (a) the amorphous and (b) the crystalline states.

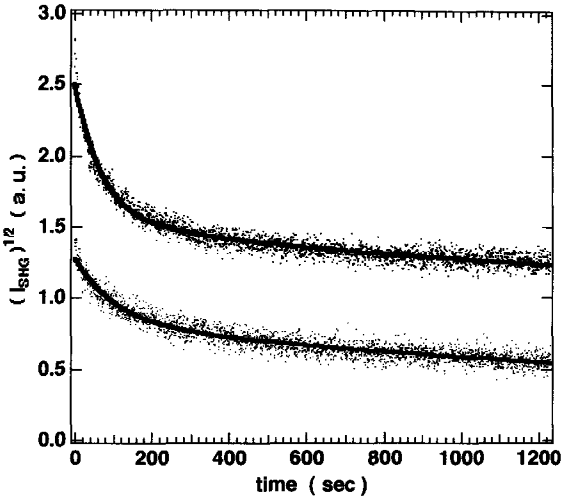

Fig. 8. Decay curves for the SHG intensity in (a) the amorphous and (b) the crystalline states. Experimental points are indicated by dots. Solid lines indicate the fitting curves.

3.4. Relaxation process in the orientation of chromophores

We next investigated the orientational relaxation process after the corona poling source is turned off. Fig. 7 shows the SHG intensity after turning off the corona discharge. One can find that the relaxation rate of the SHG intensity in the crystalline state is slower than that in the amorphous state. The difference in the relaxation rate of the SHG intensity would be attributable to the difference in the size of the free volume available for the reorientation of the mesogenic chromophores. As mentioned above, the mobility of the mesogenic chromophores in the crystalline state is suppressed compared to that in the amorphous state due to the formation of the antiparallel conformation between the mesogenic chromophores. Considering the intensity of the electric-field-induced SHG, it seems that the electric-field-induced orientational order of the mesogenic chromophores in the crystalline state is not so large as in the amorphous state. Moreover, the size of the free volume around the mesogenic chromophores in the crystalline state is hardly redistributed by the displacement of the mesogenic chromophores. As a result, the relaxation rate in the crystalline state would be slow, as found in the alignment process. On the other hand, the size of the free volume in the amorphous state would be large enough to redistribute it after turning off the corona discharge compared to that in the crystalline state.

In order to obtain more detailed aspects of the relaxation behaviour, we have carried out curve fitting analysis for the decay curves. A biexponential function

$$f(t) = A\exp(-t/\tau_A) + B\exp(-t/\tau_B)$$

or the Kohlrausch–Williams–Watts stretched exponential function [24,25]

$$f(t) = A\exp(-t/\tau_A)^{\beta_A}$$

are often used for fitting SHG decay data after removal of the poling field, and extensive discussions based on the effect of temperature, the physical aging, the dielectric relaxation of host polymers, and the decay of the surface and trapped space charges have been presented [5–13]. In this study, a biexponential function was used for fitting the SHG decay data, since we have considered that the SHG relaxation behaviour of the side-chain polymer system consists of two components owing to the coupling between the motion of the NLO chromophores and that of the polymer backbone. Table 1 gives the values of τ_A, τ_B and normalized coefficients A and B for the decay curves, and the fitting curves along with the observed curves are shown in Fig. 8.

The vertical axis represents the square root of the relative SHG intensity which is proportional to the NLO polarization. The coefficients A and B represent the contribution of each component to the decay of the SHG intensity, and τ_A, τ_B are the characteristic relaxation times. Since the initial steep decay of the SHG intensity observed in both states is attributable to the discharge of the surface and trapped space charges, a part of the initial steep decay was neglected in the curve fitting process. Moreover, we investigated the relaxation rate of the surface charges after removal of the poling field by measuring the surface voltage, because the decay rate of the SHG intensity depends on the decay rate of space charges [10–13]. We found that the surface voltage showed an exponential decay curve and the relaxation time was three orders of magnitude faster than τ_B in Table 1. Therefore, the decay of the surface charge is considered to have little effect on the SHG relaxation process after the initial steep decay in this case. This is attributable to the weak applied voltage and short time period of applying the corona discharge.

As can be found from Table 1, the decay curve of the SHG intensities in both states clearly consists of two components. One is the fast relaxation component and the other

Table 1
Parameters obtained by fitting biexponential function for square root of SHG intensity decay data

State	A	τ_A (s)	B	τ_B (s)
Amorphous	0.37	1404	0.63	70
Crystalline	0.63	3099	0.37	113

is the slow relaxation component. Although coefficient A is smaller than coefficient B in the amorphous state, the situation is reversed in the case of the crystalline state. This means that the SHG decay process in the amorphous state is mainly governed by the fast relaxation component, whereas the slow relaxation component is a dominant factor for the SHG decay process in the crystalline state. As mentioned above, we have considered that the SHG decay behaviour in the side-chain NLO polymer consists of the relaxation in the NLO chromophores and the polymer backbone. It is considered that the fast and slow relaxation components would be tentatively assigned to the orientational relaxation of the mesogenic chromophores and the rearrangement of the conformation of the siloxane backbone, respectively. That is to say, the orientational relaxation of the mesogenic chromophores is a dominant factor in the relaxation process of the SHG intensity in the amorphous state. On the other hand, the rearrangement of the conformation of the siloxane backbone is a dominant factor in the crystalline state. The intermolecular interaction between the mesogenic chromophores in the amorphous state is weak and a sufficient free volume which is redistributed by the displacement of the mesogenic chromophores exists after turning off the corona discharge. In this case, the mesogenic chromophores can reorient without the rearrangement of the conformation of the polymer backbone. That is, the degree of the coupling between the motion of the mesogenic chromophores and the segmental motion of the siloxane backbone would be small. On the contrary, the mesogenic chromophores form the antiparallel conformation with high density in the crystalline state. Consequently, the size of the free volume around the mesogenic chromophores is small due to the strong intermolecular interaction between the mesogenic chromophores. Under such a condition, the mobility of each mesogenic chromophore is considerably inhibited, and a dramatic reorientation of each mesogenic chromophore would not be induced by applying the electric field. As a result, the antiparallel conformation of the mesogenic chromophores would be slightly lessened by the cooperative motion of the mesogenic chromophores. Furthermore, the cooperative motion of the mesogenic chromophores will lead to the change of the conformation of the polymer backbone. From the above considerations, it is considered that the motion of the mesogenic chromophores in the crystalline state is governed by the motion of the polymer backbone.

4. Conclusions

The orientational behaviour against the external electric field of the mesogenic chromophores for the thin film of the side-chain liquid crystalline polysiloxane has been investigated by monitoring the SHG intensity. For the first time, we have investigated the comparison of the orientational behaviour between the amorphous and crystalline states using the identical polymer. Although the response to the external electric field in the amorphous state could be mainly regarded as a fast response in the mesogenic chromophores, that in the crystalline state was suggested to be governed by a slow response accompanying the siloxane backbone. That is to say, it is suggested that the mesogenic chromophores in the amorphous state can move independently with other mesogenic chromophores and the degree of the coupling between the motion of the mesogenic chromophores and that of the polymer backbone would be small, whereas the situation in the crystalline state should be distinct in that the degree of the coupling between the motion of the mesogenic chromophores and that of the siloxane backbone would be large. These results were considered to be originated in the strength of the intermolecular interactions between the neighbouring mesogenic chromophores and the size of the free volume around the mesogenic chromophores.

References

[1] Williams DJ, editor. Nonlinear optical properties of organic and polymeric materials, ACS Symposium Series 233. Washington, DC: American Chemical Society, 1982.
[2] Messier J, Kajzar F, Prasad P, editors. Organic molecules for nonlinear optics and photonics. Dordrecht: Kluwer, 1991.
[3] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31.
[4] Singer KD, Sohn JE, Lalama SJ. Appl Phys Lett 1986;49:248.
[5] Hampsch HL, Yang J, Wong GK, Torkelson JM. Macromolecules 1988;21:526.
[6] Hampsch HL, Yang J, Wong GK, Torkelson JM. Macromolecules 1990;23:3640.
[7] Hampsch HL, Yang J, Wong GK, Torkelson JM. Macromolecules 1990;23:3648.
[8] Dhinojwala A, Wong GK, Torkelson JM. Macromolecules 1992; 25:7395.
[9] Dhinojwala A, Wong GK, Torkelson JM. Macromolecules 1993; 26:5943.
[10] Guan HW, Wang CH, Gu SH. J Chem Phys 1994;100:8454.
[11] Pauley MA, Guan HW, Wang CH. J Chem Phys 1996;104: 6834.
[12] Goodson T III, Wang CH. Macromolecules 1993;26:1837.
[13] Goodson T III, Gong SS, Wang CH. Macromolecules 1994;27: 4278.
[14] Schüssler S, Richert R, Bässler H. Macromolecules 1994;27:4318.
[15] Singer KD, King LA. J Appl Phys 1991;70:3251.
[16] Kaatz P, Prêtre P, Meier U, Stalder U, Bosshard C, Günter P, Zysset B, Stähelin M, Ahlhein M, Lehr F. Macromolecules 1996;29:1666.
[17] Stähelin M, Walsh CA, Burland DM, Miller RD, Twieg RJ, Volksen W. J Appl Phys 1993;73:8471.
[18] Wang H, Jarnagin RC, Samulski ET. Macromolecules 1994;27: 4705.

[19] Walsh CA, Burland DM, Lee VY, Miller RD, Smith BA, Twieg RJ, Volksen W. Macromolecules 1993;26:3720.
[20] Nemoto N, Nagase Y, Abe J, Matsushima H, Shirai Y. Macromol Chem Phys 1995;196:2237.
[21] Abe J, Hasegawa M, Matsushima H, Shirai Y, Nemoto N, Nagase Y, Takamiya N. Macromolecules 1995;28:2938.
[22] Bisle H, Romer M, Rau H. Ber Bunsenges Phys Chem 1976;80: 301.
[23] Moreno RA, Gross B. J Appl Phys 1976;47:3397.
[24] Kohlrausch R. Ann Phys (Leipzig) 1847;12:393.
[25] William G, Watts DC. Trans Faraday Soc 1970;66:80.