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Investigation of Dipolar Alignment of Mesogenic Chromophores in Side-Chain Liquid Crystalline Polysiloxane Using Electric Field Induced Second Harmonic Generation

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ABSTRACT: The behavior of the electric field induced dipolar alignment of mesogenic chromophores for a thin film of a side-chain liquid crystalline polysiloxane containing mesogenic NLO-active azo chromophores is investigated by UV−visible, polarized FTIR-ATR, variable-temperature FTIR, and second harmonic generation (SHG) measurements. This polymer exhibits a smectic C liquid crystalline phase from 59 to 113 °C, and the glass transition is observed near −19 °C. The mesogenic chromophores in the mesophase and the once-annealed solid were found to be aligned spontaneously nearly normal to the substrate (the homeotropic texture). When an electric field was applied to the once-annealed solid, a rapid increase in the SHG signal intensity was observed. It was shown that, under an electric field, the dipolar directions of the mesogenic chromophores would be easily aligned in the same direction in the once-annealed solid owing to the low T_g of the polymer, which indicates potential application for a room temperature SHG switching device.

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 quadratic hyperpolarizabilities. It is well known, however, that groups with a strong permanent dipole moment tend to form antiparallel conformations in a condensed phase including a mesophase, and this gives a centrosymmetric center in the materials and reduces the second-order nonlinear susceptibility, $\chi^{(2)}$, of the materials. One difficulty with second-order organic nonlinear optical (NLO) materials is that most of these organic compounds crystallize in a centrosymmetric space group and $\chi^{(2)}$ vanishes in spite of the high microscopic optical nonlinearity. Because of their potential applications in integrated optics, polymeric NLO materials have been the subject of extensive investigation during the past decade.[1−4] Due to the ease in processability and flexibility, polymeric materials, either doped or covalently bonded with NLO chromophores have been widely accepted as promising candidates for future applications. By incorporating these molecules into a polymer host and then applying a strong electric field, one can remove the centrosymmetry and obtain the second-order NLO materials.[5] In a typical poling experiment, the material is heated to an elevated temperature in the presence of a strong electric field and then cooled to below the glass transition temperature (T_g) of the host polymer, maintaining the electric field. The T_g must be high enough to ensure that alignment will be preserved for subsequent long-term use under ambient conditions, so poling must be carried out at a high temperature as well.[6−10]

In general, linear polysiloxane derivatives have a low T_g. Therefore, siloxane backbones have seldom been used for second-order NLO materials, because relaxation of the dipolar orientation of the second-order NLO moieties occurs due to their low T_g. Polysiloxanes have been applied for second-order NLO materials only as a backbone of the polymeric Langmuir−Blodgett film owing to their hydrophobicity.[11−14] On the other hand, polysiloxanes are often used as a polymer backbone of side-chain liquid crystalline polymers for the purpose of providing relatively stable liquid-crystalline phases in the low-temperature range.[15−19] Also polysiloxanes might be suitable for room temperature fast optical switching for future applications because molecular mobility originates in their low T_g. In this case, low-T_g materials are more desirable than high-T_g materials which suppress an alignment relaxation of NLO chromophores. Applying an electric field in the mesophase, the dipolar directions of mesogenic chromophores would be considered to align in the same direction. It is necessary to investigate the behavior of the electric field induced dipolar alignment of the mesogenic chromophores and the time response to an electric field. Information on the director alignment of the mesogenic chromophores could be obtained by various methods, for example, X-ray diffraction and spectroscopic measurement. However, it is difficult to obtain the information on the dipolar directions by these techniques. The intensity of a second harmonic generation (SHG) is sensitive to the dipolar direction. It is considered that the SHG measurement of the side-chain liquid crystalline polysiloxanes would provide information on the

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Scheme 1

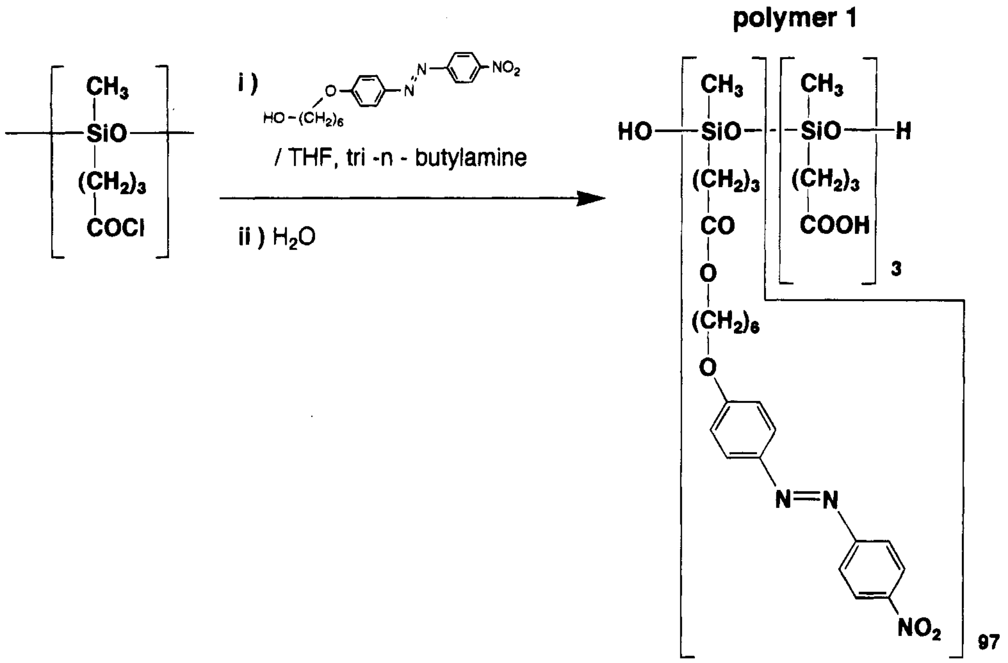

Table 1. Molecular Weights and Thermal Properties of Polymer 1

$M_n \times 10^{-3}$ [a]	M_w/M_n [b]	T_g (°C)	phase transitions[c] (°C)
2.43	1.75	−19	K 59 Sc 113 I

[a] Determined by GPC using a polystyrene-calibrated column set. [b] Polydispersity index. [c] Determined from DSC measurements, polarized microscopic observation, and X-ray diffraction measurements.

dynamics of the mesogenic chromophores in the solid and the mesophase. The poling dynamics and relaxation of polar order in guest–host polymers and covalently functionalized amorphous nonlinear optical polymers have been reported by several authors.[20–25] Very few investigations, however, have been carried out on the poling behavior in the solid state or mesophase of the side-chain liquid crystalline polysiloxanes.

In this article, the behavior of the electric field induced dipolar alignment of the mesogenic chromophores for a side-chain liquid crystalline polysiloxane containing mesogenic NLO-active azo chromophores is investigated by UV–visible, polarized FTIR-ATR, variable-temperature FTIR, and SHG measurements under an applied electric field.

Experimental Section

Materials. The side-chain-functionalized polysiloxane (polymer 1) was prepared by the esterification of poly[(3-(chlorocarbonyl)propyl)methylsiloxane] with 4-[(4-((6-hydroxyhexyl)oxy)phenyl)azo]nitrobenzene. The introduction ratio of chromophores into the side chain of polysiloxane was more than 97 mol % ($M_n = 2.43 \times 10^3$, $M_w/M_n = 1.75$). Details of preparation have been published elsewhere.[26,27] Polymer **1** exhibited liquid crystallinity, as deduced from DSC measurements, polarized microscopic observation, and X-ray diffraction measurements.[27] It was identified that polymer **1** shows a smectic C phase between 59 and 113 °C. Table 1 summarizes the thermal properties of polymer **1**.

Film Preparation. Polymer films were prepared by spin coating from a solution with a concentration of approximately 5 wt % polymer **1** in THF. The solution was first passed through a 0.50 μm filter (Millipore) to remove particle impurities. A thin, optically clear film (~1 μm thick) was prepared on a substrate by spinning at 2000 rpm. The spin-coated samples were placed in a vacuum oven at ~30 °C for over 24 h to obtain solvent-free films. For the SHG measurements, an ITO glass and a polyimide-coated ITO glass (E.H.C. Co., Ltd.) were used as substrates.

Corona Poling and *in situ* SHG. The corona discharge method was used to pole the sample, and a negative voltage of 10 kV was applied to a sharp tungsten needle located 25 mm in front of the grounded electrode onto which the polymer film was coated. A grounded hot stage for the assembly allowed for temperature variation.

The setup for SHG measurement was identical to that used in our previous work.[27] Basically, it consists of a Q-switched Nd:YAG laser operated at 10 Hz. The laser beam, the power of which was controlled by neutral-density filters, was directed through a λ/4 waveplate and a plate polarizer to be converted to the p-polarized beam. The sample holder was placed on a rotating stage and rotated around a horizontal axis. A p-polarized laser beam passed through a UV–visible light cutoff filter was focused on the sample film. After the sample, an infrared-absorbing filter and an analyzer were used to detect only the p-polarized SH signal at the monochromator entrance. At the monochromator exit slit, the SH signal was detected by a PM tube and processed with a boxcar integrator which was interfaced to a personal computer.

Results and Discussion

Identification of the Directions of the Mesogenic Chromophores for the Film Sample by UV–Visible and FT-IR Spectra. Figure 1 shows the temperature dependence of the UV–visible absorption spectra obtained by the transmission method for identical films (~1 μm thick) spin cast on a quartz substrate. The UV–visible absorption spectrum in THF measured between 300 and 600 nm and two kinds of different spectra for the solid state, solid **A** and solid **B**, are given in this figure. Solid **A** was a once-annealed sample which was heated to the mesophase temperature, and solid **B** was a sample without heat treatment.

The absorbances of solid **A**, solid **B**, the mesophase, and the isotropic phase are considerably different. The spectral changes owing to the phase transitions were found to be reversible. The absorption band at ~370 nm could be assigned to the π–π* transition band of the 4-nitro-substituted azobenzene chromophores, and the electric dipole transition moment oriented nearly

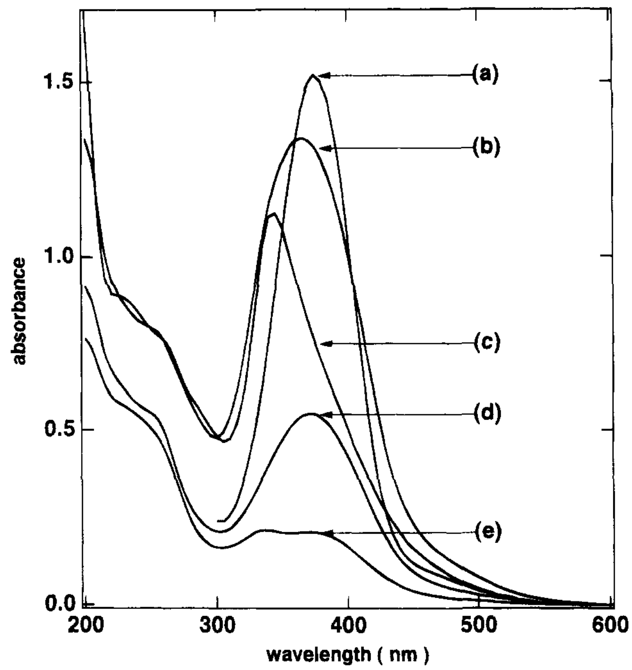

Figure 1. UV–visible absorption spectra of (a) a THF solution of polymer **1** (5.0×10^{-3} wt %, light path length is 10 mm) and the (b) isotropic phase, (c) solid **B**, (d) mesophase, and (e) solid **A** of polymer **1** spin cast on a quartz substrate (film thickness: ~1 μm).

along the molecular long axis.[28] That is, the π–π^* transition of the azo dye chromophore is polarized along the molecular long axis, and when the electric vector of the light is parallel to the direction of the molecular long axis, the molecule absorbs light intensely. Therefore, considering the direction of the electric vector of the light, this difference of the absorption band at ~370 nm can be explained by the difference of the orientation of the mesogenic chromophores against the substrate. When the direction of the mesogenic chromophores is more perpendicular with regard to the substrate's surface, the transition moments of the chromophores are oriented more normal to the film. Since transmitted light normal to the surface has its electric vector parallel to the film, its interaction with the mesogenic chromophores is reduced and the resulting spectra show both a decrease in intensity and a wavelength shift. Therefore, the mesogenic chromophores in both the solid **A** and the mesophase are considered to be more perpendicular to the substrate, and the tilt angle of the mesogenic chromophores becomes small in the solid **A** compared with that of the mesophase. In contrast to these states, the mesogenic chromophores in the solid **B** and the isotropic phase are randomly distributed in the thin film of the polymer. The shapes of their absorption bands are considerably different, and this would be attributable to the difference in molecular interactions in their states; however, it is beyond the scope of this article to discuss the subject in further detail. It is concluded that the mesogenic chromophores can align spontaneously nearly perpendicular to the substrate only by heat treatment. These findings were also confirmed by measuring polarized FTIR-ATR spectra and variable-temperature FTIR (VT-FTIR) spectra as shown below.

Figure 3 shows polarized FTIR-ATR spectra of the same spin-coated film used in the above measurements, and the spectra of the solid **A** and the solid **B** are given. A schematic of the polarized FT-IR ATR measurement and the incident IR electrical vector is shown in Figure 2. A ZnSe crystal was used for an internal reflection element (IRE). No difference was found in the spectra for the solid **B** by alternating the IR electrical vector. This means that the mesogenic chromophores in the solid **B** are randomly aligned, and this result is consistent with the above discussion. In the spectra of the solid **A**, the relative intensities of the 1520 and 1350 cm^{-1} bands changed largely according to the direction of the IR electrical vector. These bands could be tentatively assigned to the asymmetric and symmetric stretching vibrations of the nitro group, respectively. Moreover, the behavior of the intensity of the ring-stretching mode of the phenyl group observed at ~1600 cm^{-1} was similar to that of the symmetric stretching vibration of the nitro group. From these results, we could obtain detailed information about the orientation of the mesogenic chromophores. The direction of the vibrational transition moment for the symmetric and asymmetric stretching vibrations of the nitro group could be roughly estimated as schematically shown in Figure 4, and that for the ring-stretching vibration of the para substituted benzene could be considered to be parallel to that of the symmetric stretching vibration of the nitro group.

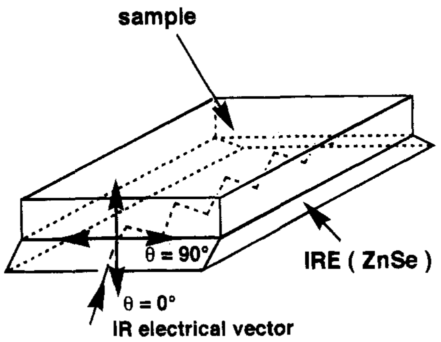

Figure 2. Polarization angle of the IR electrical vector for FTIR-ATR measurements.

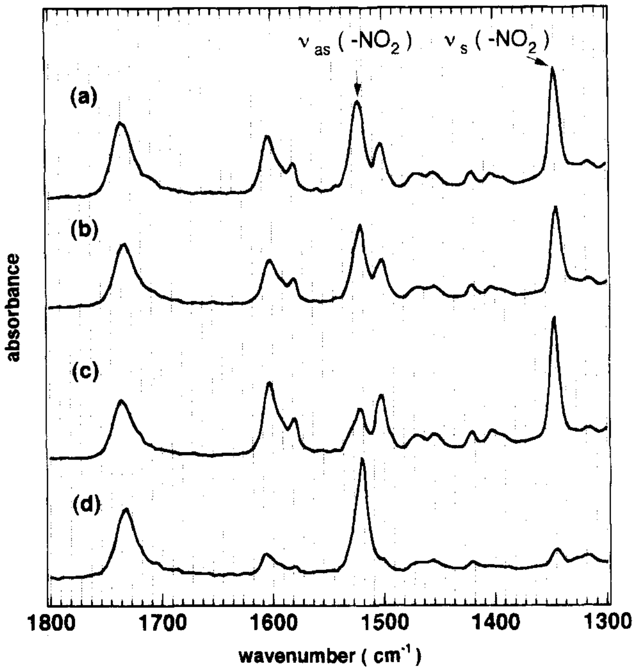

Figure 3. FTIR-ATR spectra of (a) solid **B** ($\theta = 0°$), (b) solid **B** ($\theta = 90°$), (c) solid **A** ($\theta = 0°$), and (d) solid **A** ($\theta = 90°$). θ represents the angle of the incident IR electrical vector with regard to the substrates surface as shown in Figure 2.

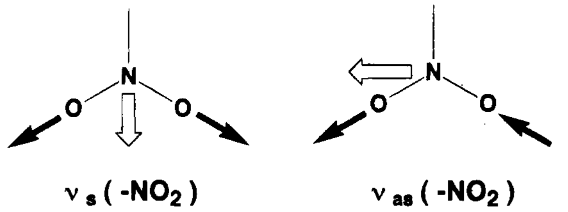

Figure 4. Direction of the vibrational transition moment for the symmetric and asymmetric stretching vibrations of the nitro group.

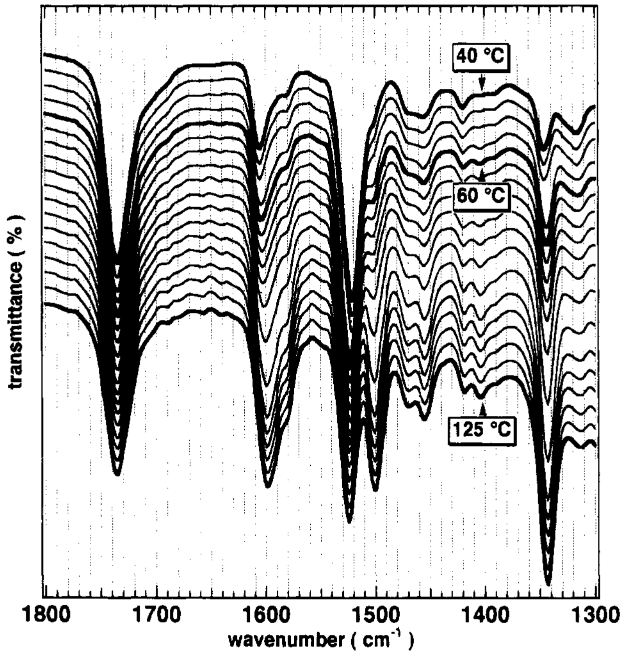

Figure 5. Variable-temperature FTIR spectra of polymer **1** spin cast on an Ag-evaporated substrate, (film thickness: ~1 μm). These spectra were measured in the range 40−125 °C at 5 °C intervals during the heating process by the reflection method.

From these considerations, the intensity dependence of the FTIR-ATR spectra on the direction of the IR electrical vector can be clearly explained by assuming that the mesogenic chromophores aligned nearly perpendicular to the substrate. That is, when the direction of the IR electrical vector is parallel to the substrate ($\theta = 90°$), the absorption intensity for the asymmetric stretching vibration of the nitro group is enhanced; on the other hand, when the direction is perpendicular to the substrate ($\theta = 0°$), the absorption intensities for the symmetric stretching vibration of the nitro group and the ring-stretching vibration of the phenyl group are enhanced. These spectra also support the conclusion which was drawn on the basis of the measurements of the UV−visible spectra.

VT-FTIR spectra of the film on an Ag-evaporated substrate obtained by the reflection method are shown in Figure 5. These spectra were measured in the range 40−125 °C at 5 °C intervals during the heating process. The IR electrical vector was parallel to the surface, as was the case in the measurements of the UV−visible spectra. The spectral changes were also reversible with the variation of temperature. The arrangement of mesogenic chromophores is also supported by these spectra. The difference in the tilt angle of the mesogenic chromophores against the substrate between the solid **A** and the mesophase is understandable on the basis of the difference in the relative intensity of the 1520 and the 1350 cm^{-1} bands in their phases.

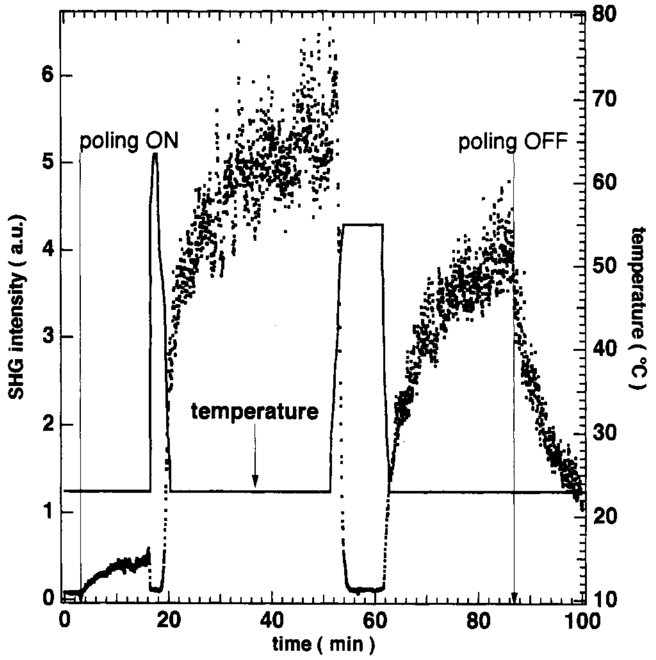

Figure 6. Dependence of the SHG intensity of the spin-cast film of polymer **1** on temperature and application of electric field. An ITO glass is used as a substrate. The pulse energy of the fundamental light is 1.74 mJ.

Behavior of the Electric Field Induced Dipolar Alignment of the Mesogenic Chromophores. To study the thermal behavior of the electric field induced dipolar alignment of the mesogenic chromophores, the temperature dependence of the SHG signal from the film sample was monitored. The corona discharge method was used to pole the sample, and a negative voltage of 10 kV was applied to a sharp tungsten needle located 25 mm in front of the polymer film surface. It is known that surface charges accumulate at the surface of a polymer film during corona poling.[29] In this way a large electrostatic field is created in the film that interacts with the polar chromophores. The electrostatic field aligns the dipole in the direction of the poling field, which leads to dichroism.[30] The SHG signal at an incidence angle of 45° was chosen.

The time profile of the SHG intensity at various temperatures is shown in Figure 6. When no electric field was applied to the solid **B**, only a very weak SHG signal was detected. Considering the results of the UV−visible and FTIR spectra of this state, the interpretation of this observation could be considered as follows. The mesogenic chromophores are randomly aligned in the solid **B**, and the second-order nonlinear susceptibility, $\chi^{(2)}$, of the material is very small in spite of having a high microscopic optical nonlinearity. When the electric field was applied to the solid **B**, the SHG signal gradually increased, and the intensity of the signal was saturated soon. It is particularly noteworthy that the SHG signal vanished immediately by raising the temperature to the mesophase. This phenomenon indicates that the mesogenic chromophores are aligned so as to have an inversion center and lower $\chi^{(2)}$ in the mesophase; in other words, the mesogenic chromophores take an antiparallel conformation. In general, it is possible to control the directions of the mesogenic chromophores by an external electric field, while the dipolar directions of the mesogenic chromophores of this polymer cannot be aligned in the same direction under an electric field. From the measurements of the surface potential in the mesophase with the corona poling

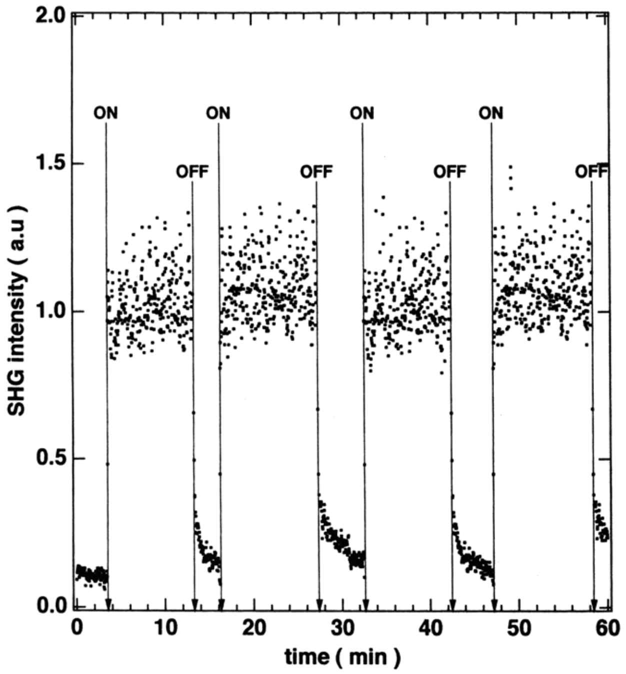

Figure 7. Dependence of the SHG intensity in the solid **A** of the spin-cast film of polymer **1** on application of an electric field. A polyimide-coated ITO glass is used as a substrate. The pulse energy of the fundamental light is 1.74 mJ.

treatment, it was found that an ionic current was caused and the surface potential was not applied. This may be due to small amounts of ionic impurities. This ionic current was not observed in the solid state. By considering the mobility of the siloxane backbones in the mesophase, it is reasonable to explain the difference of the surface potential between the mesophase and the solid state by the ionic current. We have tried to remove the ionic impurities; however, it was not possible to remove them completely.

When heating was discontinued and the film was cooled to room temperature under an electric field, a drastic enhancement of the SHG signal was observed. The polymer shows the solid state at room temperature; however, the solid state was transformed from the solid **B** into the solid **A** by this heat treatment. It should be noted that the inversion center of the mesogenic chromophores found in the mesophase has been removed in the solid **A** by the electric field. That is, in the solid **A**, the dipolar directions of the mesogenic chromophores can be easily aligned in the same direction under the electric field.

The above experiments were carried out using an ITO glass substrate, and the material did not exhibit a fast time response to an external electric field as was expected from a molecular mobility originating in their low T_g. It is considered that the time response may be dependent on the surface effect of the substrate. From this point of view, we investigated the surface effect of the time response using a polyimide-coated ITO glass substrate. Figure 7 shows the time profile of the SHG intensity under various applied voltages in the solid **A**. It can be seen that the SHG signal undergoes a rapid increase on applying the corona poling and a rapid decrease by breaking the electric field. This fast time response is particularly surprising in view of the fact that the phase of the polymer is not a mesophase but a solid phase. We considered that this would be ascribable to their low T_g. That is to say, even at the room temperature, siloxane backbones are considered to have enough mobility to align the mesogenic chromophores. Though a detailed mechanism of the surface effect is not clear at present, it is shown that the side-chain liquid crystalline polysiloxanes are applicable to a SHG switching device.

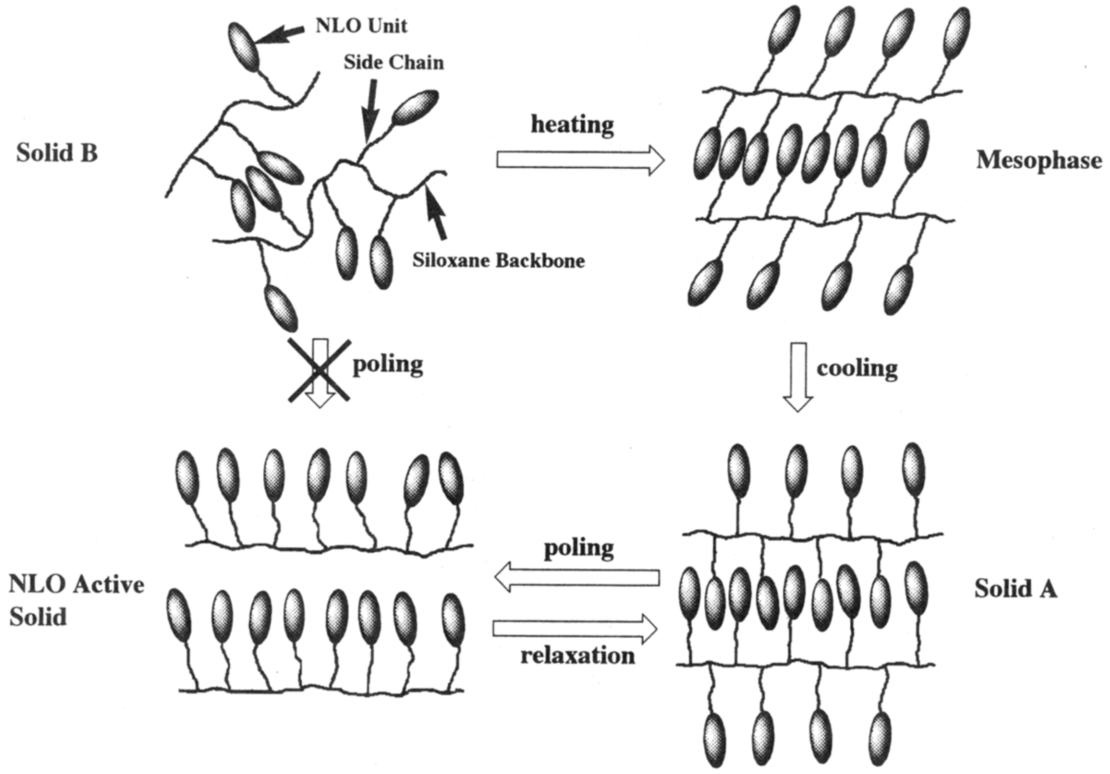

Figure 8. Schematic for the behavior of the electric field induced dipolar alignment of the mesogenic chromophores of polymer **1**.

Conclusion

The electric field induced dipolar alignment of mesogenic chromophores for the side-chain liquid crystalline polysiloxane has been investigated. From the UV–visible, FTIR-ATR, and VT-FTIR spectra, it is found that, in both the solid **A** and the mesophase, the azo dye mesogenic chromophores are aligned nearly perpendicular to the substrate, and the tilt angle from the orthogonal vector of the substrate surface of the mesogenic chromophores becomes slightly smaller in the solid **A** compared with that of the mesophase. The dipolar directions of the mesogenic chromophores can be aligned in the same direction in the solid **A** under the electric field; however, this is not the case with the solid **B**. This difference in the solid state could be ascribable to the difference in the alignment condition of the mesogenic chromophores between them. The spectroscopic data have shown that the mesogenic chromophores in the solid **B** are randomly aligned and the solid **B** has an isotropic feature. In the solid **B**, it is considered that a cooperative motion of the mesogenic chromophores is difficult, and the dipolar directions of the chromophores can not be aligned well under the electric field. On the other hand, when the mesogenic chromophores are aligned in the same direction as shown in the solid **A**, the electric field can easily induce the cooperative motion of these chromophores so as to align in the same direction. The mobility of the mesogenic chromophores in the solid state are considered to originate in the low T_g.

The behavior of the electric field induced dipolar alignment of the mesogenic chromophores for polymer **1** are summarized in Figure 8.

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