Supramolecular Polar Thin Films Built by Surfactant Liquid Crystals: Polarization-Tunable Multilayer Self-Assemblies with In-Plane Ferroelectric Ordering of Ion-Based Dipoles

Akihiko Kanazawa, Tomiki Ikeda,* and Jiro Abe[†]

Contribution from the Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan and Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

Received September 7, 2000. Revised Manuscript Received December 5, 2000

Abstract: Polar order in the phosphonium liquid crystal thin films, which are composed of two-dimensional ion-pair-based domains separated by the insulating hydrocarbon layers, was probed by second harmonic generation (SHG) analysis. Despite the ordinary amphiphilic self-assemblies containing no π-electron moieties, the solid-state thin films retaining a smectic layer structure showed clearly an SHG activity, while the disordered films without the layer structure were not active at all for the SHG. It was found that the multilayer structure plays a crucial role for the SHG from the phosphonium thin films and the ionic layers act as an SHG-active site. The most significant characteristic of this system is to possess an ability to control SHG intensity electrically. The efficiency of the SHG process in the thin-film assemblies was enhanced by applying an external electric field parallel to the layer plane. Furthermore, through evaluation of thermal stability of the sample films, it was revealed that the SHG signals were detected only in the solid-state temperature range and the disappearance of the SHG occurs earlier than the solid-to-liquid crystalline phase transition. These results demonstrated that the origin of polar order in the phosphonium thin films is due to in-plane noncentrosymmetric arrangement (ferroelectric ordering) of ion pairs as an electric dipole, that is, dipole symmetry in an ionic layer.

Introduction

Structurally controlled thin-film assemblies offer many attractions for the construction of new functionalized materials with unique structures, in which it is essential to control the structure of organizations at the molecular or atomic levels. For instance, for optoelectronic materials in device applications such as sensors and memories, the key requirement is the presence of noncentrosymmetric (polar) order. In the molecule-based systems, the materials can possess an optoelectronic function only when the noncentrosymmetric molecules are incorporated into a noncentrosymmetric macroscopic structure. The achievement of such macroscopic ordering (i.e., dipolar alignment), however, is a formidable task, since the permanent electric dipoles of noncentrosymmetric molecules tend to pair in opposite directions to give rise to a centrosymmetric macroscopic structure. In fact, the attribute of polar order is usually restricted to a certain crystalline class.

Supramolecular assembly (including liquid crystals, which has been regarded as one of the most promising groups of materials for applications in optoelectronic devices[1]) is a current topic. To generate the spontaneous dipolar alignment by employing supramolecular architecture several approaches have been conducted thus far, which include the Langmuir−Blodgett,[2] silane coupling,[3] intercalation,[4] polymerization,[5] and self-assembly[6] techniques as well as the introduction of chirality[7] and a liquid crystalline property[8,5b] into a molecular system. In the conventional supramolecular systems, the macroscopic polar order emerges from the molecule-based dipolar alignment, so that their characteristics as optoelectronic materials may greatly

---

* To whom correspondence should be addressed. Telephone: +81-45-924-5240. Fax: +81-45-924-5275. E-mail: tikeda@res.titech.ac.jp. URL: http://www.res.titech.ac.jp/polymer.

[†] Tokyo Metropolitan University.

(1) (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89−112. (b) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*, VCH: Weinheim, 1995; pp 89−138. (c) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155−173.

(2) (a) Ashwell, G. J.; Jackson, P. D.; Crossland, W. A. *Nature* **1994**, *368*, 438−440. (b) Wijekoon, W. M. K. P.; Wijaya, S. K.; Bhawalkar, J. D.; Prasad, P. N.; Penner, T. L.; Armstrong, N. J.; Ezenyilimba, M. C.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 4480−4483. (c) Sundari, S. S.; Dhathathreyan, A.; Kanthimathi, M.; Nair, B. U. *Langmuir* **1997**, *13*, 4923−4925. (d) Bune, A. V.; Fridkin, V. M.; Ducharme, S.; Blinov, L. M.; Palto, S. P.; Sorokin, A. V.; Yudin, S. G.; Zlatkin, A. *Nature* **1998**, *391*, 874−877. (e) Yam, V. W.-W.; Yang, Y.; Yang, H.-P.; Cheung, K.-K. *Organometallics* **1999**, *18*, 5252−5258.

(3) (a) Lin, W.; Yitzchaik, S.; Lin, W.; Malik, A.; Durbin, M. K.; Richter, A. G.; Wong, G. K.; Dutta, P.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1497−1499. (b) Lin, W.; Lin, W.; Wong, G. K.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 8034−8042. (c) Yang, X.; McBranch, D.; Swanson, B.; Li, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 538−540.

(4) Coradin, T.; Clément, R.; Lacroix, P. G.; Nakatani, K. *Chem. Mater.* **1996**, *8*, 2153-2158.

(5) (a) Kauranen, M.; Verbiest, T.; Boutton, C.; Teerenstra, M. N.; Clays, K.; Schouten, A. J.; Nolte, R. J. M.; Persoons, A. *Science* **1995**, *270*, 966−969. (b) Trollsås, M.; Orrenius, C.; Sahlén, F.; Gedde, U. W.; Norin, T.: Hult, A.; Hermann, D.; Rudquist, P.; Komitov, L.; Lagerwall, S. T.; Lindström, J. *J. Am. Chem. Soc.* **1996**, *118*, 8542−8548. (c) Tew, G. N.; Li, L.; Stupp, S. I. *J. Am. Chem. Soc.* **1998**, *120*, 5601−5602.

(6) Kondo, T.; Horiuchi, S.; Yagi, I.; Ye, S.; Uosaki, K. *J. Am. Chem. Soc.* **1999**, *121*, 391−398.

(7) (a) Kim, O.-K.; Choi, L.-S.; Zhang, H.-Y.; He, X.-H.; Shih, Y.-H. *J. Am. Chem. Soc.* **1996**, *118*, 12220−12221. (b) Verbiest, T.; Elshocht, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913−915.

(8) (a) Wang, H.; Jin, M. Y.; Jarnagin, R. C.; Bunning, T. J.; Adams, W.; Cull, B.; Shi, Y.; Kumar, S.; Samulski, E. T. *Nature* **1996**, *384*, 244−247. (b) Walba, D. M.; Dyer, D. J.; Sierra, T.; Cobben, P. L.; Shao, R.; Clark, N. A. *J. Am. Chem. Soc.* **1996**, *118*, 1211−1212. (c) Espinet, P.; Etxebarría, J.; Folcia, C. L.; Ortega, J.; Ros, M. B.; Serrano, J. L. *Adv. Mater.* **1996**, *8*, 745−748.

10.1021/ja003302+ CCC: $20.00

originate from the electronic property of the organic molecule itself. In most cases, the organic molecules used as an optoelectronic active component are synthesized according to a common molecular design, in which electron-donating and -withdrawing groups are connected through conjugated π-electron moieties. Such molecules thus are colored because of a bathochromic shift of the intramolecular charge-transfer absorption band. This often causes a serious problem on practical applications of the organic materials. For instance, in nonlinear optical applications, the low transparency to visible light causes destruction of the materials by the nonlinear absorption.

With regard to the noncolored optoelectronic materials, there are many inorganic polar crystals such as barium titanate and sodium nitrite which are representative ferroelectrics. Such nonmolecule-based materials show a spontaneous polarization (*P*s) as an overall permanent electric polarization in the absence of an external field such as an electric field and a mechanical stress.[9] The *P*s is due to a noncentrosymmetric structure resulting from the spontaneous displacement of ions or the ordering of the dipole groups.[9] In the inorganic polar materials, the thin-film assemblies can be prepared by a variety of physical and chemical techniques such as laser ablation, evaporation, sputtering, chemical vapor deposition, and sol−gel processing.[9e,f] However, it is often difficult not only to manipulate the atomic arrangement in a given material but also to prepare the thin films with large-scale perfect domains without a structural defect. Since the crystalline materials are mainly used as sources of the thin-film assemblies, the assembly structures are usually limited by the intrinsic single-crystal structures of the crystalline sources.

More recently, we showed the preliminary result on the polar order in ion-based liquid crystal thin films,[10] which are solid-state multilayer organizations self-formed by phosphonium surfactant complexes as a novel class of thermotropic ionic liquid crystals consisting of an ion pair of positive phosphorus and negative chloride atoms as well as double hydrocarbon chains (see Figure 1).[10b,11] Through the evaluation of spatial arrangement of ions in the phosphonium thin-film assembly by means of second-order nonlinear optics, we found that the phosphonium self-assembly can be regarded as a polar thin film produced by two-dimensional ionic layers with a polar order (Figure 1a). In a two-dimensional ionic layer within the phosphonium assembly, it was assumed that *P*s occurs parallel to the ionic layer because of the spontaneous displacement of ions, that is, the noncentrosymmetric atomic arrangement. The generation of *P*s in the layer plane, namely, may be due to the collective effect of each pair of positive and negative ions as an electric dipole. Through the theoretical calculations, the spontaneous displacement of ions in the ionic layer was revealed to be ascribed to the variety of bonding manner (i.e., the characteristic electronic structure) of phosphorus atom (Figure 1b).

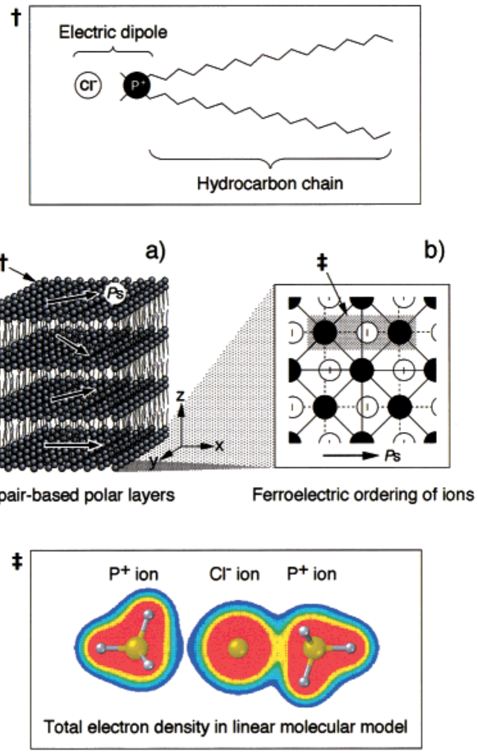

Figure 1. Schematic representation of the polar thin film produced by the liquid crystalline surfactant complex: (a) solid-state layered thin film consisting of two-dimensional self-assembled ionic layers with spontaneous polarization (*P*s) which are stacked parallel to the glass substrates ($x-y$ plane); (b) realized relative arrangement of ions in an ionic layer on the basis of the simplest square array model in which black and white circles correspond to the positive phosphorus and negative chloride ions, respectively; (†) chemical structure of the phosphonium liquid crystal used in this study; (‡) total electron density obtained through theoretical calculation on the linear $[PH_4-Cl-PH_4]^+$ model.

Such phosphonium liquid crystal thin films, which are colorless and transparent, entirely differ from the conventional supramolecular polar assemblies because the existence of macroscopic polarization is not due to an alignment of molecules having dipole moments, but due to a noncentrosymmetrical arrangement of ions (i.e., ferroelectric ordering of ion pairs as an electric dipole). On the basis of the preliminary results, the phosphonium thin films can be considered "quasi-ferroelectrics" consisting of two-dimensional domains with the *P*s. In the present study, we explored the origin of polar order in the phosphonium liquid crystal films in more detail by second harmonic generation (SHG) spectroscopy as an effective tool to probe the polar structure in a material. Furthermore, we attempted to align the *P*s in each domain into one direction by application of an external electric field and to extend the phosphonium surfactants to polarization-tunable optoelectronic materials.

Experimental Section

Materials. The chemical structure of the phosphonium salt (dimethyldioctadecylphosphonium chloride) possessing thermotropic enantiotropic liquid crystalline property used in this study is shown in Figure 1. This compound was synthesized by the method reported previously[11a] and characterized by means of ^{1}H NMR spectroscopy (Bruker, AC200), fast atom bombardment mass spectrometry (FABMS; JEOL, JMS-AX

---

(9) (a) Kittel, C. *Introduction to Solid State Physics*, 5th ed.; John Wiley & Sons: New York, 1976; pp 413−417. (b) Smolenskii, G. A.; Bokov, V. A.; Isupov, V. A.; Krainik, N. N.; Pasynkov, R. E.; Sokolov, A. I. *Ferroelectrics and Related Materials*; Taylor, G. W., Ed.; Gordon and Breach Science Publishers: New York, 1984. (c) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, 1994; pp 765−766. (d) Ibach, H.; Lüth, H., Eds. *Solid-State Physics*, 2nd ed.; Springer: Berlin Heidelberg, 1995; Chapter 11. (e) Li, C.-Y.; Xu, Y. In *Handbook of Photonics*; Gupta, M. C., Ed.; CRC Press LLC: Florida, 1997; pp 87−124. (f) Ramesh, R., Ed. *Thin Film Ferroelectric Materials and Devices*; Kluwer Academic Publishers: Massachusetts, 1997.

(10) (a) Kanazawa, A.; Ikeda, T.; Abe, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 612−615. (b) Kanazawa, A.; Ikeda, T. *Mater. Res. Soc. Symp. Proc.* **1999**, *559*, 201−210.

(11) (a) Kanazawa, A.; Tsutsumi, O.; Ikeda, T.; Nagase, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7670−7675. (b) Kanazawa, A.; Ikeda, T. *Coord. Chem. Rev.* **2000**, *198*, 117−131. (c) Kanazawa, A.; Ikeda, T.; Nagase, Y. *Chem. Mater.* **2000**, *12*, 3776−3782.

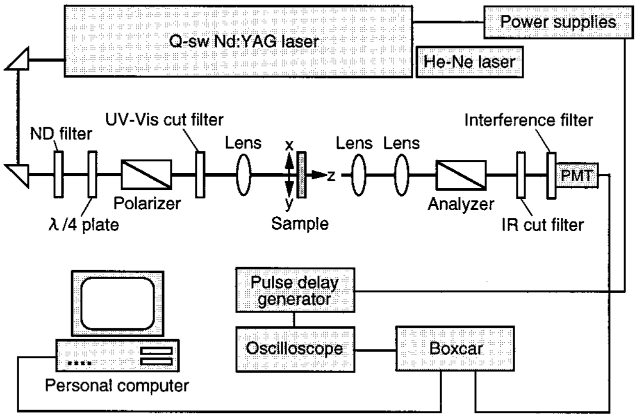

Figure 2. Experimental setup for the SHG measurement.

505W), elemental analysis (for C, H, and Cl atoms), inductively coupled plasma (ICP) analysis (for P atom), and high-performance liquid chromatography (HPLC; Shimadzu, HIC-6A) in which an analytical column (Shimadzu, Shim-pack IC-C3) for nonsuppressor ion chromatography was used.[11a] Through the analytical investigation, the phosphonium chloride synthesized was confirmed to be free from ionic and nonionic impurities because of the identification limit on the impurities. In addition, the phosphonium salt was reconfirmed to show the smectic A phase based on the bilayer stacking (see Figure 1a), in which homeotropic structure is formed spontaneously, in the temperature range from 82 to 145 °C on heating and from 142 to 58 °C on cooling at a scanning rate of 1 °C min^{-1} by differential scanning calorimetry (DSC; Seiko I&E, SSC-5200 and DSC220C), polarizing optical microscopy (Olympus, Model BX50; Mettler, FP82HT hot stage and FP90 central processor), and powder X-ray diffractometry (MAC Science, MXP^3, equipped with a thermal controller, model 5301).

Preparation of the Thin-Film Assemblies. For the SHG measurement, solid-state thin films retaining a smectic layer structure or an isotropic phase structure could be readily prepared by injecting the phosphonium salt into a sandwiched cell with a gap ranging from 2 to 20 μm in the isotropic phase, followed by rapid quenching from the appropriate fluid phase to room temperature so as to give the solid state. In the sample preparation, we used glass substrates coated with a pattern of interdigitated indium−tin-oxide (ITO) electrodes as one substrate of a sandwiched cell, in which the distance between the electrodes is 50 μm and the electrodes are 50 μm wide, and applied the lateral electric field (E_{ex}, 0.1 dc V/μm) to the sample along the *x* axis in Figures 1 and 6 since the ionic layers are stacked parallel to the glass substrates ($x-y$ plane). The phosphonium thin films prepared were colorless because of the perfect transparency to visible light.

The observation of the solid-state samples using a polarizing optical microscope provided us with the information on the molecular arrangement. In all of the samples, no light could absolutely transmit through a pair of crossed polarizers irrespective of the polarized direction of probe light. We observed no optical textures due to birefringence of the samples. This result implies that the initial fluid phases, which are uniform homeotropic or isotropic states, before rapid cooling in the sample preparation are completely frozen through the quenching process. Such thermal treatment did not also result in appearance of micrometer-sized crystals. Furthermore, to evaluate the degree of interlayer ordering in the phosphonium self-assemblies, a sample film for the X-ray measurement was prepared by casting a phosphonium solution in chloroform onto a common glass substrate, followed by quenching to room temperature after annealing at the liquid crystalline temperature. The film thickness was estimated to be about 2 μm with a film-thickness monitor (Sloan, DEKTAK 3030). The sample film prepared was subjected to the X-ray diffraction analysis in the thin-film method (Rigaku, RINT 2500V).

SHG Measurements. Figure 2 shows an experimental setup for the SHG measurements used in this study. A Q-switched Nd:YAG laser (Spectron, SL404G; $\lambda = 1064$ nm, 10-Hz repetition rate, 6-ns pulse duration) was used as the light source. The laser beam, the pulse energy of which was controlled with neutral-density filters (HOYA), was passed through a one-quarter waveplate (multiple order quartz retardation plate, Oriel) and a Glan-laser polarizer (Oriel) to convert to the laser beam polarized along the *x* axis or the *y* axis in Figures 1 and 6. The sandwiched cell was placed on a sample stage and a polarized laser beam passed through a UV−visible light cutoff filter (HOYA) was focused by a first quartz lens (Sigma Koki) on the sample along the *z* axis, that is, perpendicular to the $x-y$ plane (glass substrates). The incident light including the SH light (532 nm) generated from the sample was collimated by a second quartz lens (Sigma Koki), and then was focused again by a third quartz lens (Sigma Koki). An analyzer as a second Glan-laser polarizer (Oriel), an infrared-cut filter (HOYA), and an interference filter (CVI) were used to detect only the SH light (532 nm) with a certain polarized direction. The detection system consists of a photomultiplier tube (PMT; Hamamatsu, R329-02) and a boxcar averager (Stanford Research, SR250). The PMT voltage was set to 1600 V by a PMT high-voltage supply (Stanford Research, PS325). The output signal was amplified to a detectable level and was monitored by a digitizing oscilloscope (Tektronix, 2445B). The width of the boxcar gate was set to about 50% of the width of the output pulse from the PMT. The SHG signal, which was detected with a PMT and processed with a boxcar integrator, was interfaced to a personal computer.

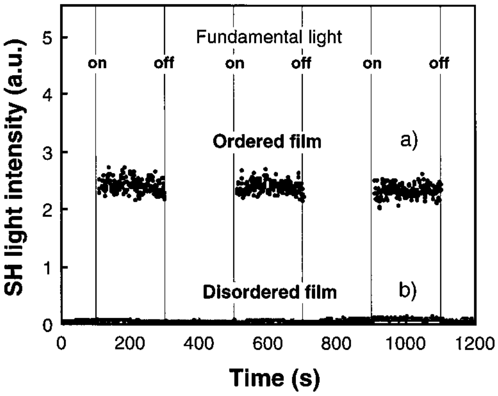

Figure 3. Change in the intensity of SHG signals on irradiation of the fundamental light observed for the phosphonium thin films: (a) ordered sample retaining a smectic layer structure, (b) disordered film without layer structures.

To investigate structural phase transition of the two-dimensional self-assembled ionic layers with polar order within the phosphonium thin film (i.e., disappearance of the ferroelectric ordering by solid−solid transition), the polarization-treated 15-μm-thickness sample after application of the electric field was heated from room temperature to liquid crystalline temperature at a heating rate of 5 °C min^{-1} using a thermal controller (Mettler, FP82HT hot stage and FP90 central processor), and the SH light intensity was measured simultaneously as a function of time. The SHG measurement was performed under the same conditions as those described above.

Results and Discussion

Emphasis of Layered Structure on Polar Order in the Thin Film. In the preliminary results reported previously, we inferred that the SHG from the phosphonium liquid crystal thin film could be ascribed to the nonlinear polarization in a two-dimensional ionic layer.[10] To verify this hypothesis again, we used at first the 15-μm-thickness films before application of an electric field and investigated the influence of layer structure on the SHG behavior. Figure 3 exhibits change in the SH light intensity observed for the sample films with different phase structures. The SHG signals were clearly observed for the ordered thin film retaining a smectic character (Figure 3a). On the other hand, the disordered thin film without a layer structure was not active at all for the SHG (Figure 3b). It is obvious that the layered structure plays a crucial role for the second-order nonlinear optical property of the phosphonium thin-film as-

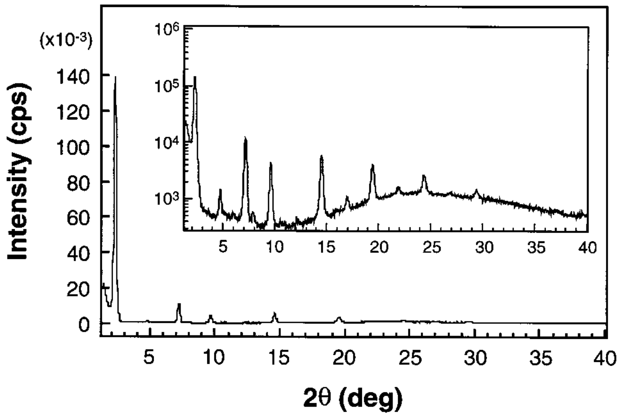

Figure 4. X-ray diffraction patterns of the solid-state phosphonium thin film measured at room temperature. (Inset) Diffraction patterns of logarithmic intensity of diffraction peaks versus diffraction angle for the same sample.

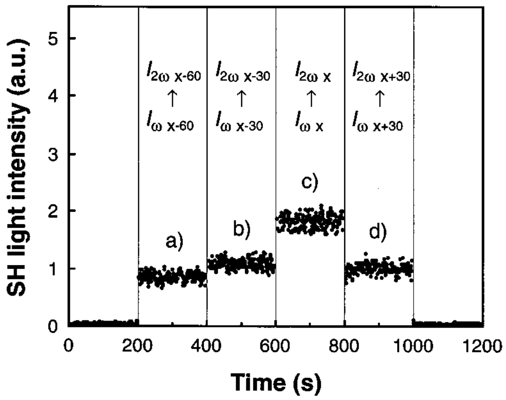

Figure 5. Effect of the polarized direction of fundamental light on the SHG activity. In (c), $I_{\omega\ x}$ and $I_{2\omega\ x}$ correspond to the intensity of fundamental and SH waves with the polarized direction along the *x* axis in Figure 1, respectively. When the fundamental light with the polarization plane rotated from the *x* axis at every ±30 ° around the *z* axis was employed, the SHG signals displayed in (a), (b), and (d) were observed.

semblies. Additionally, we confirmed that the signals detected as an SH wave include no fluorescence from the phosphonium molecules due to the multiphoton absorption process. If the phosphonium molecules exhibit the 1064-nm-induced fluorescence around at 532 nm, the light green color should not be monochromatic. In fact, no signal was absolutely observed when an interference filter with a central wavelength at 490, 510, or 570 nm (fwhm, 3 nm) was used instead of the normal interference filter to detect only 532-nm light in the SHG measurement (see Figure 2). Consequently, we concluded that the light emission from the phosphonium self-assembly is attributed to the SHG process.

The interlayer and intralayer orientational order of the phosphonium thin film was evaluated by the X-ray diffraction analysis in the thin-film method. The X-ray diffraction patterns obtained are shown in Figure 4. The smectic layer spacing calculated from the lowest diffraction angle was 37.1 Å. The calculated molecular length in their most extended configuration was 18.5 Å, when the counteranion was not taken into account. The layer thickness determined by the X-ray measurement corresponds to a 2-fold molecular length of the phosphonium salt. Furthermore, in the high-angle region, the diffraction pattern also gave several peaks which contain information on the internal order within a layer plane. These results clearly indicate that the phosphonium assembly possesses not only a highly aligned multilayer structure based on the bilayer stacking even in the solid state but also an ordered structure in the two-dimensional ionic layers. The manner of atomic arrangement in an ionic layer could not be examined quantitatively; however, it is at least true that a certain ordering of ions exists in the layer plane and leads to the nonlinear polarization for the SHG.

The unique feature of the phosphonium thin film is the existence of the macroscopically ordered *P*s in the absence of an external electric field, even though each ionic layer is separated by the insulating glassy alkyl segments (see Figure 1a). This is evident from the angular dependence of the polarization plane of fundamental light on the SHG activity as shown in Figure 5. When the fundamental wave polarized along the *x* axis was employed, the thin-film assembly was most active in the SHG. On the other hand, with the fundamental light possessing the different polarization planes rotated around the *z* axis, the SH light intensity decreased with increasing rotation angle. This result indicates that the phosphonium thin film would have no perfect orderliness of the *P*s in each ionic layer as shown in Figure 1a. However, it is not well understood at the present stage of research how the polar order is communicated between the layers.

With respect to the efficiency of the SHG process, the SHG from the phosphonium thin film with a thickness of 15 μm was referenced to the SHG from a Y-cut quartz crystal with a thickness of 1.1 mm. The maximum intensity of the SHG signals from the sample film was approximately 1% of quartz. We have demonstrated that, in the theoretical calculations for the simplest linear molecular models, the phosphonium chloride gives a bistable geometry with the noncentrosymmetric atomic arrangement, arising from the participation of 3*d* orbitals of the phosphorus atom in a weak P−Cl bond formation (see Figure 1). In this model, the potential barrier was approximately 0.5 kcal/mol.[10a] Such order-of-magnitude calculation reveals that the chloride ion might overcome the barrier so as to give a centrosymmetric atomic arrangement even at room temperature, since the estimated potential barrier is low. Thus, each ionic layer within the films would not have perfect noncentrosymmetric structure like an inorganic polar crystal. By designing a phosphonium molecule with an efficiency to show a higher-potential barrier, therefore, the phosphonium liquid crystal films are expected to become more active for the SHG.

Polarization Treatment by Application of Lateral Electric Field. A lateral electric field was applied to the phosphonium thin film along the *x* axis by using substrates with a pattern of interdigitated electrodes, and we attempted to rearrange the ions in the layer plane (Figure 6). As shown in Figure 7, when the fundamental light polarized along the *x* axis was employed, the 15-μm-thickness thin film was more SHG-active than that before application of the electric field. In contrast, with irradiation of the fundamental light polarized along the *y* axis, the SHG signals were almost not observed. These results suggest that the *P*s in each ionic layer can be aligned by applying electric field, resulting in the enhancement of polar order in the thin film (see Figure 6). If the observed phenomenon is truly induced by the application of an electric field, the efficiency of the polarization treatment should be dependent on the strength of an applied electric field. As shown in the inset figure in Figure 8, the interdigitated electrodes give an uneven electric field to the sample film. The line of electric force is parallel to the ionic layer plane at the central position between the positive and negative electrodes, resulting in the most effective electric field

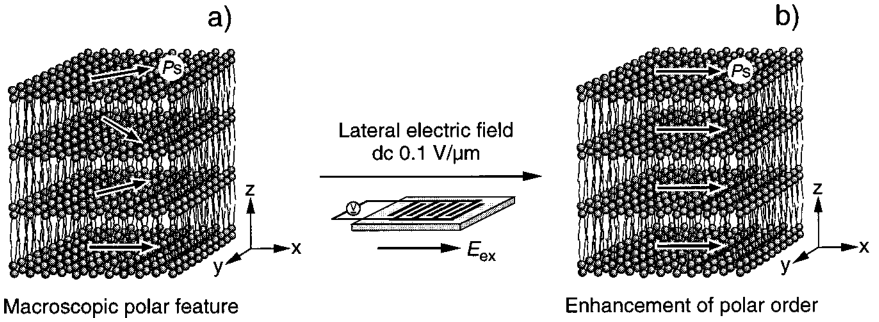

Figure 6. Unidirectional alignment of the spontaneous polarization (*P*s) achieved by application of the lateral electric field (E_{ex}, 0.1 dc V/μm): (a) a sample film before application of the electric field, (b) a phosphonium thin film with polar order enhanced through the polarization treatment.

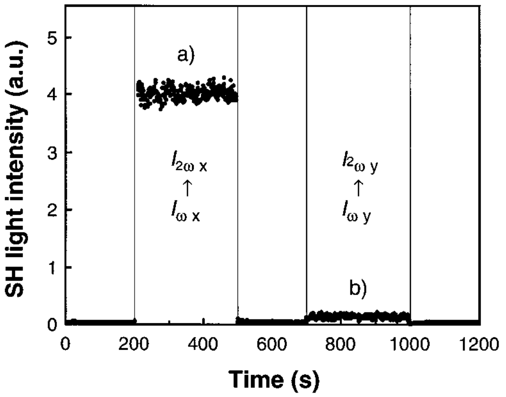

Figure 7. Change in the SH light intensity on irradiation of the fundamental light observed for the polarization-treated sample film with the ordered *P*s: (a) with the fundamental light polarized along the *x* axis; (b) with the fundamental light polarized along the *y* axis.

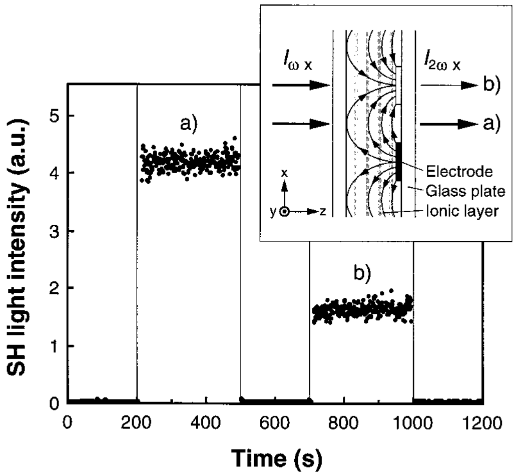

Figure 8. Effect of the irradiation point of the fundamental light polarized along the *x* axis on the SHG intensity in the polarization-treated sample: (a) at the central position between the electrodes, (b) on the electrode. (Inset) Black and white squares indicate positive and negative electrodes, respectively, and a curved arrow corresponds to the line of electric forces in the applied electric field.

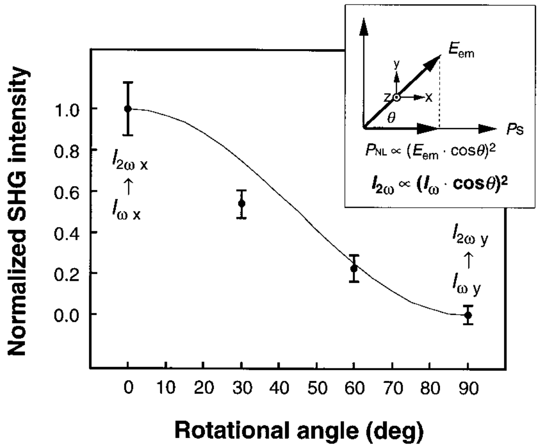

Figure 9. Angular dependence of the polarization plane of the fundamental wave on the SHG activity. The polarized directions (θ) at 0° and 90° are parallel to the *x* axis and the *y* axis in Figure 6, respectively: (●) experimental data, (−) theoretically fitted curve.

for the polarization treatment. On the other hand, on the electrodes, the ionic layers perceive a weak electric field across the layer plane. In fact, the SHG intensity was affected by the incident position of the fundamental light (Figure 8). There is a possibility that the extent of polar order in the phosphonium thin films can be controlled through the polarization treatment.

The validity of the electrical response of the polar order is also evident from the fact that the SH light intensity depends on the polarized direction of the fundamental wave as shown in Figure 9. The polarized directions at 0° and 90° are parallel to the *x* axis and the *y* axis in Figure 6b, respectively. When the electromagnetic field E_{em} of the fundamental wave makes an angle θ with the *x* axis, the projection of E_{em} on the *x* axis is $E_{em}\cdot\cos\theta$ which should be an efficient electromagnetic field for the SHG. Since the nonlinear polarization is proportional to the square of the electromagnetic field,[12] the SH wave ($I_{2\omega}$) generated by the polarized fundamental wave (I_ω) can be written as $I_{2\omega} \propto [I_\omega\cdot\cos\theta]^2$. The theoretically fitted curve using this equation is given as a solid line in the figure. As described in Figure 9, the observed values of the SHG intensity agreed approximately with the theoretical values. This result therefore demonstrates that the *Ps* in each ionic layer within the phosphonium thin film could be realigned into one direction by application of an external electric field. Furthermore, the effect of film thickness on the SHG behavior of the phosphonium assembly was investigated for the polarization-treated samples with different film thickness from 2 to 20 μm. Within the electric dipole approximation, the SH light intensity generated in a thin film can be written as $I_{2\omega} \propto [\chi^{(2)}]^2 \propto [N]^2$, where $\chi^{(2)}$ and N are the macroscopic nonlinearity and the film thickness (i.e., the number of layers), respectively.[12] Thus, the intensity of SHG signals should show a quadratic increase with increasing film thickness. Actually, we confirmed that the best fit to the experimental data points yields a straight line with a slope of approximately 2 (Figure 10). The fulfillment of the equation described above indicates that the phosphonium thin films are composed of the ionic layers with the uniform *P*s directions (see Figure 6b).

---

(12) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1994.

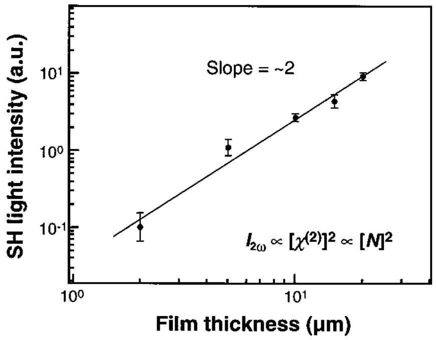

Figure 10. SHG intensity in the polarization-treated samples with different film thickness.

Ferroelectrics are characterized by the existence of polarization hysteresis loops, namely, the *P*s directions should be changed by the external field such as an electric field and a mechanical stress.[9] Although the phosphonium thin film provides aligned *P*s through the polarization treatment, there is no conclusive evidence to show its ferroelectric property. Unfortunately, no polarization hysteresis loop could be observed for the phosphonium thin films. However, it is evident that the phosphonium thin film shows the electrical response of polar order, leading to the saturation of electric polarization. On the basis of the simplest test for the ferroelectricity, therefore, it may be reasonable that the phosphonium thin films are regarded as "quasi-ferroelectrics" which are composed of the two-dimensional domains with the *P*s.

Origin of the Polar Order in the Phosphonium Thin Films. The interaction of the molecule with an electromagnetic field of light is described as the perturbation Hamiltonian. The interaction Hamiltonian can be written as a multipole expansion by a canonical transformation: $H_{\mathrm{I}} = -(\mu \cdot E + m \cdot H + Q \cdot \nabla E + \cdots)$, where μ, m, and Q correspond to the electric dipole, magnetic dipole, and electric quadrupole moments of the molecules, respectively.[13] Within the electric dipole approximation, SHG is allowed in a molecular organization with dipole symmetry (i.e., dipolar order) but forbidden in one with quadrupole symmetry (e.g., antiparallel array of the dipolar molecules). In the latter case, SHG should be dominated by electric quadrupole and magnetic dipole contributions. In fact, the smectic A films, which are prepared from the conventional cyanobiphenyl-based liquid crystals with the dipole moments along the molecular long axis, have been reported to show the SHG activity.[14] It has been concluded that the nonlinear optical response is due to the antiparallel orientational order of the molecules in each smectic layer, that is, the smectic A films have quadrupole rather than dipole symmetry.[14] Furthermore, it has been also demonstrated that the nondipolar molecules, in which charge transfer is multidirectional rather than dipolar in character, possess the second-order nonlinear optical property due to octupolar noncentrosymmetric structure.[15] Even in the nonpolar molecular systems, therefore, the SHG can be observed on the basis of the quadrupole or octupole processes.

It is easy to imagine that the ionic layer within the amphiphilic multilayer assemblies possesses the alternate arrangement of positive and negative ions, that is, the antiparallel packing of dipoles (quadrupole symmetry). If the quadrupole process contributes to the generation of SH wave in the phosphonium liquid crystals, the other ionic liquid crystals should be also active in the SHG. However, it has been confirmed that the analogous thin films, which are formed by the ammonium liquid crystal with the positive nitrogen ions instead of the positive phosphorus ions, are inactive at all for the SHG.[10a] We have predicted therefore that the SHG from the phosphonium thin film originates from the customary dipole process due to the ferroelectric ordering of ion pairs as an electric dipole (see Figure 1). In this study, it was found that the polar order in the liquid crystal films is enhanced by the application of the lateral electric field. If the SHG is ascribed to a quadrupole process, such an enhancement of the polar order may not be observed. These results therefore support our argument that the second-order nonlinear optical property of the phosphonium thin films is governed by the electric dipole process.

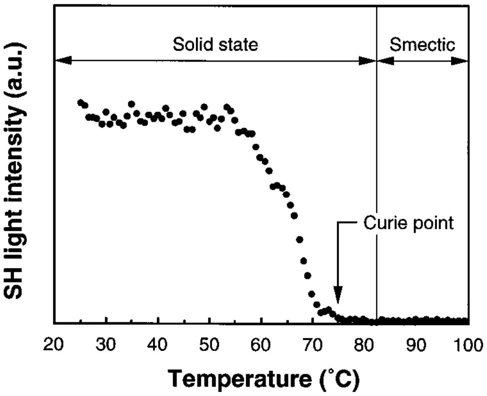

Figure 11. Temperature dependence of the SHG from the phosphonium thin film with ordered *P*s.

In the case of the smectic A films with a quadrupole symmetry described above, the SHG can be observed even in the fluid phase possessing a macroscopic centrosymmetric structure.[14] On the other hand, the materials with a dipole symmetry no longer exhibit SHG activity in the fluid phase because of the disruption of ferroelectric ordering of dipoles (i.e., noncentrosymmetric structure). Actually, when the usual inorganic polar crystals with a noncentrosymmetric structure are heated, the macroscopic polarization disappears at a certain temperature (i.e., Curie point), resulting from the increase of lattice vibration.[9] In the solid-state thin films used in this study, therefore, the SHG can be predicted to disappear below solid-to-liquid crystalline phase-transition temperature. Figure 11 indicates the temperature dependence of SH light intensity observed for the polarization-treated sample film. The decrease of the SHG intensity began at 55 °C, and the sample film became SHG-inactive at 75 °C. It was revealed that the phosphonium thin film shows no SHG activity not only in the smectic A phase but also in the solid-phase, retaining a smectic layer structure in the temperature range of 75−82 °C. The disruption of dipolar order in the ionic layers seems to occur earlier than the solid-to-liquid crystalline phase transition. This result may be powerful evidence to show the presence of in-plane spontaneous polarization arising from the dipole process.

Conclusions

We have shown for the first time that multilayer self-assemblies, which are formed by phosphonium liquid crystals as a structurally simple surfactant, act as polarization-tunable polar thin films through the evaluation of their SHG properties.

---

[13] Chemla, D. S.; Zyss J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, 1987; Vol. 1, pp 63−72.

[14] Hsiung, H.; Shen, Y. R. *Phys. Rev. A* **1986**, *34*, 4303−4309.

[15] (a) Ledoux, I.; Zyss, J.; Siegel, J. S.; Brienne, J.; Lehn, J.-M. *Chem. Phys. Lett.* **1990**, *172*, 440−444. (b) Zyss, J.; Dhenaut, C.; Chauvan, T.; Ledoux, I. *Chem. Phys. Lett.* **1993**, *206*, 409−414. (c) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Bozec, H. L. *Nature* **1995**, *374*, 339−342.

In the phosphonium thin-film assemblies, it was found that a layered structure, which is built up from alternating layers of ions and alkyl segments, plays a significant role for the SHG. This result supports our prediction that the SHG-active site is a two-dimensional ionic layer separated by the insulating glassy alkyl layers, which possesses *P*s as a permanent electric polarization because of the noncentrosymmetric array (ferroelectric ordering) of ion pairs as an electric dipole. It is worth mentioning that the SHG activity increased by application of an external electric field (i.e., polarization treatment), indicating the enhancement of polar order in the phosphonium thin films. The electrically enhanced polar order was assumed to be due to the unidirectional alignment of the *P*s in each two-dimensional ionic domain. Furthermore, the phosphonium thin films showed the structural phase transition (i.e., order−disorder solid−solid phase transition) and became SHG-inactive even in the solid-state temperature range. These results clearly indicate that the SHG from the phosphonium assemblies is governed by the electric dipole process based on the ferroelectric ordering of ion pairs.

The thin-film assemblies presented in this study can be regard as a novel class of the supramolecular polar systems. Because the phosphonium thin films are mixed organic/inorganic materials in which features of the organic and inorganic components, corresponding to the flexible hydrocarbon chains and the ion-based electric dipoles, respectively, complement each other, leading to unique solid-state structures and materials with the permanent electric polarization. In the future, we will explore new functionality of the phosphonium thin films except the second-order nonlinear optical property (such as ferroelectric, piezoelectric, pyroelectric, or electrooptical properties) and try their applications as optoelectronic materials.

JA003302+