

Variations in Polymeric Structure of Ferroelectric Poly(vinylidene fluoride) Films During Annealing at Various Temperatures

Masahiro Inoue,¹ Yasunori Tada,^{1*} Katsuaki Suganuma,¹ Hiroshi Ishiguro²

¹The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

²Department of Adaptive Machine systems, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Received 10 August 2008; accepted 29 September 2008

DOI 10.1002/app.29323

Published online 3 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To clarify the thermal degradation mechanisms of uniaxially drawn poly(vinylidene fluoride) (PVDF) films, variations due to annealing in the polymeric structures of the films were investigated using the small-angle X-ray scattering (SAXS) and Fourier transform infrared (FTIR) spectroscopy. The films were composed of lamellar crystals that were stacked perpendicular to the stretch direction. Although the crystallinity of the films decreased during annealing in the temperature range above the preannealing temperature, the lamellar structure was maintained even after the annealing process. There are two kinds of irreversible relaxation mechanisms during the annealing process of the films, including both a decrease in crystallinity within the lamellae and also thick-

ening of the lamellae. A significant lamella thickening effect was observed when the films were annealed above $\sim 100^\circ\text{C}$. FTIR spectra suggested some disordered structures are developed during thickening of the lamellae. Furthermore, a long-range periodic structure was formed in the films that were annealed above the melting temperature of PVDF. The polymeric structures formed during the fabrication process (including high-order structures and disorders in molecular conformation) were clarified as having a significant influence on the annealing behavior of ferroelectric PVDF films. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2837–2843, 2009

Key words: annealing; disorder; lamellar; SAXS; FTIR

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) or tetrafluoroethylene (TFE) are well known as typical ferroelectric polymers.^{1–3} The β -phase of PVDF is especially important for the realization of piezoelectric effects, since it has an all-transconformation structure, resulting in a net dipole moment.^{4,5} However, PVDF films often form the nonpolar α -phase when they are fabricated using the melt crystallization or solution cast techniques. Therefore, mechanical stretching is generally utilized to obtain the β -phase. Although PVDF-based polymers can exist in a single crystal form,^{6,7} in most cases they are provided in a semicrystalline form in which the crystalline phases form a lamellar structure.^{8,9}

From the viewpoint of application of PVDF films, the thermal stability and annealing behavior of these films is an important issue because the temperature

ranges for assembly process and for applications are limited because of the thermal degradation in piezoelectricity of these films. To discuss the thermal degradation mechanisms of these films, variations in polymeric structure of these films during annealing at elevated temperatures need to be clarified.

The present authors discussed the relationship between the thermal stability of PVDF films and the preannealing condition in a previous article.¹⁰ As a result, it was clarified that the piezoelectricity of the films significantly deteriorates because of crystal relaxation during annealing above the preannealing temperature because the content of the ferroelectric β -phase decreases, accompanied by shrinkage of the film. In fact, the piezoelectricity decreased in proportion to the decrease in the content of the β -phase in the temperature range below $\sim 100^\circ\text{C}$. However, the ratio of the decrease in the piezoelectricity was apparently large compared with that for the content of the β -phase above $\sim 100^\circ\text{C}$. Therefore, it was suggested that there are additional relaxation mechanisms above $\sim 100^\circ\text{C}$. In addition, several thermodynamically nonequilibrium phenomena were observed during annealing above the preannealing temperature. Unfortunately, the origin of these phenomena which are induced during the annealing process still remains unclear.

*Present address: Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466-8555, Japan.

Correspondence to: M. Inoue (inoue@sanken.osaka-u.ac.jp).

In most of the previous works in this subject area, the majority of researchers have focused on information concerning the ordering of polymer chains in the crystal phases as obtained from wide-angle X-ray diffraction (WAXD) studies to analyze the PVDF films.^{3–5,8} However, clarifying in high-order structures (such as the lamellar structure) is considered to be essential to discuss the degradation mechanisms during the annealing process from the viewpoint of the concerted dynamics of polymer chains. For example, the high-order structures significantly affect the diffusion behavior of polymer chains because of their topological nature.^{11–15} Although WAXD is effective for analyzing the crystal structure and crystallinity, it cannot provide information on the long-range ordered structures. The small-angle X-ray scattering (SAXS) technique can be a complement to WAXD because it can provide structural information in the range from 1 to 100 nm. In addition, the Fourier transform infrared (FTIR) spectroscopy can provide structural information concerning the molecular structures (molecular conformation) and molecular packings in polymeric materials. By combining the information from these analytical techniques, we can comprehensively discuss the polymeric-structural features in PVDF films. In the present work, variations in the polymeric structures in a uniaxially drawn PVDF film during annealing at various temperatures are examined using SAXS and FTIR to discuss the annealing behavior of the PVDF film.

EXPERIMENTAL

Uniaxially drawn PVDF films (Measurement Specialties Inc., PIEZO FILM: 28 μm in thickness) which included Ag electrodes that were prepared by a screen-printing process were used as the specimens in the present work. The Ag electrodes were carefully wiped away from the PVDF films using acetone. The manufacturer had already annealed the films at 60°C during the fabrication process. Several specimens of the PVDF films were additionally annealed at 40–200°C for 1 h. During the annealing process, the films were placed between metal blocks to maintain their planarity. After finishing the annealing process, the specimens were rapidly cooled in air. Subsequently, the SAXS (Cu $K\alpha$ radiation: 50 kV, 250 mA; detector distance: 300 mm) spectra of these films were measured in the scattering angle range between 0.1 and 4° by using transmitted X-rays. The FTIR spectra were also measured in the wavenumber range of 400–1000 cm^{-1} at ambient temperature. In addition, films that had been annealed at 100 and 120°C were subsequently annealed at 80–160°C for 1 h to examine variations in their SAXS profiles. The WAXD analyses of the

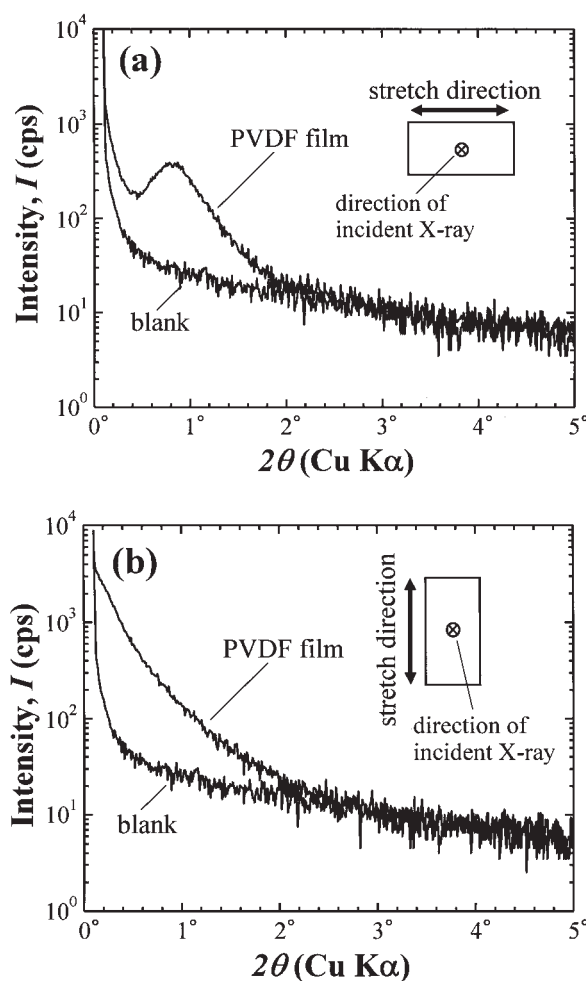


Figure 1 SAXS profiles of a PVDF film preannealed at 60°C obtained from two different incident directions.

films were also conducted using Cu $K\alpha$ radiation (50 kV, 200 mA).

RESULTS AND DISCUSSION

Structural characterization of PVDF films preannealed at 60°C

Figure 1(a,b) show the SAXS profiles of a PVDF film preannealed at 60°C. The horizontal axis indicates the scattering angle (2θ) that is related to the magnitude of the scattering vector (q), as represented in eq. (1):

$$q = 4\pi \sin \theta / \lambda \quad (1)$$

where λ is the wavelength of the X-rays.

In the case of Figure 1(a), the X-rays were incident to the film specimens in the direction shown in this figure. A broad peak indicating a long-range periodic structure is detected between 0.5 and 1.7° in 2θ . This peak in the SAXS profile is attributed as originating from the lamellar structure of the crystalline phase (stacked lamellar structure)¹⁶ in the PVDF

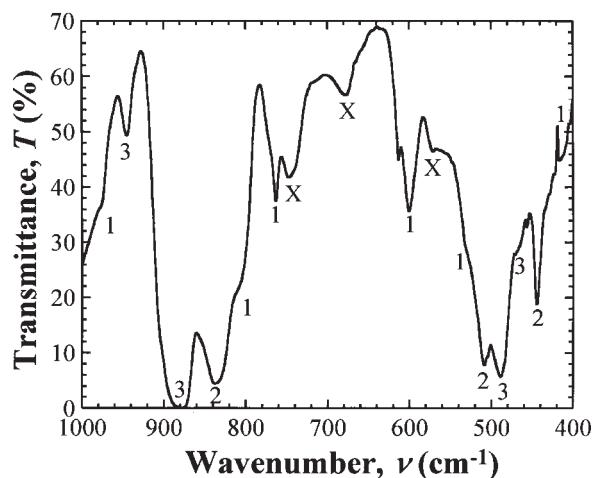


Figure 2 FTIR spectrum of a PVDF film preannealed at 60°C. The absorption bands are categorized into four groups; 1: group 1 (α -form), 2: group 2 (β -form), 3: group 3 (both forms), X: disordered structures.

film. The average lamella thickness (d) can be estimated from the scattering angle of the peak top ($2\theta_{\text{top}}$) using the Bragg's equation;

$$d = \lambda / 2 \sin \theta_{\text{top}} \quad (2)$$

By contrast, no long-range periodic structure was observed in the SAXS profile when the film was rotated 90° in the in-plane direction from the position in Figure 1(a), as shown in Figure 1(b). Hence, the lamellar structure is considered to be orientated perpendicular to the stretch direction. The PVDF film was confirmed to be mainly composed of the ferroelectric β -form crystal phase using WAXD.¹⁰ The crystalline phase is clarified to form a lamellar structure that is orientated perpendicular to the stretch direction in the PVDF film by using SAXS.

On the other hand, the FTIR can provide structural information concerning molecular conformation. Figure 2 shows the FTIR spectrum of film preannealed at 60°C. The infrared absorption bands can be categorized into three groups.^{17–19} Groups 1 and 2 are limited to the α -form (alternating trans and gauche sequences; TGTG⁻) and to the β -form (all-trans planar zigzag conformation; TT), respectively. Group 3 of the absorption bands is observed in both forms. Because strong absorption bands (840, 510, 445 cm^{-1}) that are categorized into group 2 are clearly observed in Figure 2, the FTIR spectrum supports the results of WAXD analysis reported in a previous article.¹⁰ However, some bands that are not assigned to the optically active fundamentals of the regular crystal lattice of the α - and β -forms^{8,17,18} are clearly observed in the FTIR spectrum (as indicated as X in Fig. 2). These bands are attributed to disorders in molecular conformation. For example, the band that is observed around 675 cm^{-1} is considered

to be assigned to a localized mode associated with the head-to-head or tail-to-tail units in the crystalline region.¹⁸ At least, the crystalline region in this film seems to contain some disorders in molecular conformation.

Polymeric-structural variations in the PVDF films during postannealing

Figures 3(a,b) show the SAXS profiles of films preannealed at 60°C after annealing at 80–160°C for 1 h. When the films were annealed at 40, 50, and 60°C for 1 h, hardly any variations in the SAXS profile were observed (not shown here).

The lamellar structure is maintained even after annealing at a temperature above the preannealing temperature, although a decrease in crystallinity due to annealing was detected by WAXD in these films in this temperature range (Fig. 4). However, the average lamella thickness varied significantly during

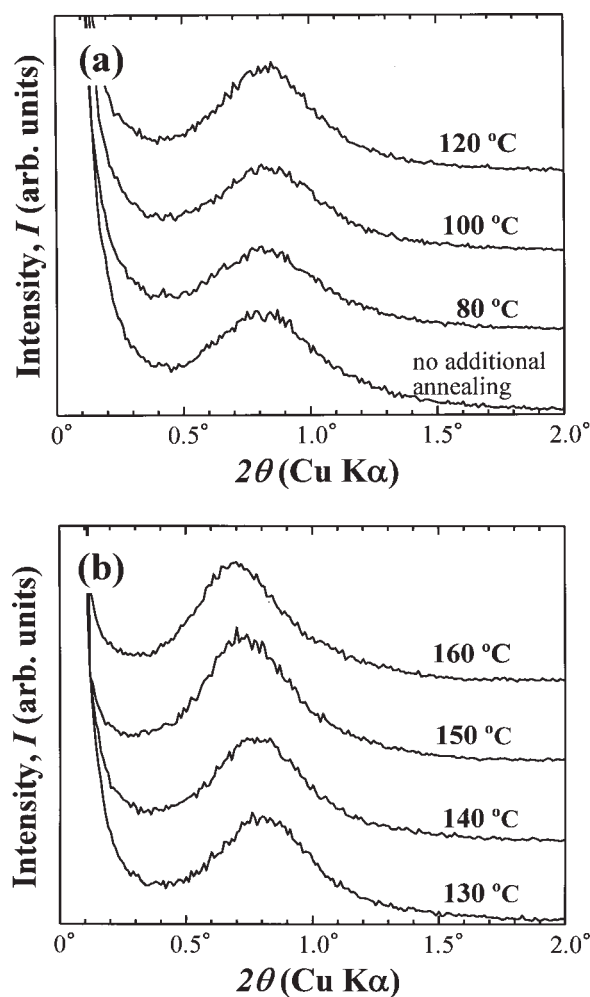


Figure 3 SAXS profiles of the PVDF films preannealed at 60°C after annealing at (a) 40–120°C and (b) 130–160°C for 1 h.

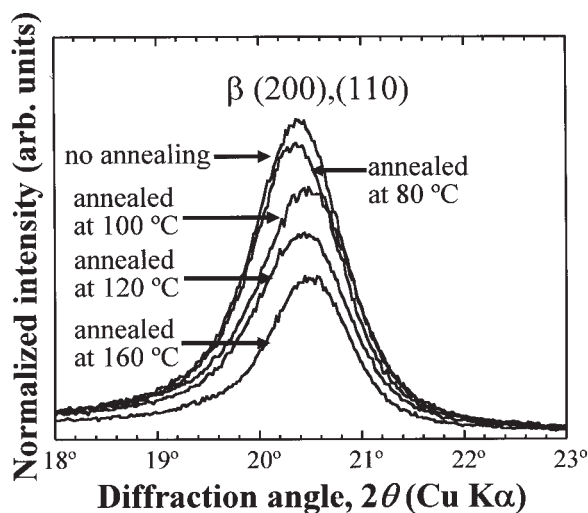


Figure 4 WAXD patterns of the PVDF films preannealed at 60°C before and after annealing at 80, 100, 120, and 160°C for 1 h.

the annealing process. Figure 5 shows the average lamella thickness that was estimated using the SAXS profiles as a function of annealing temperature. The average lamella thickness decreases slightly in the temperature range between 80 and ~100°C because of annealing. By contrast, the thickness increases significantly with increasing annealing temperature when the annealing was conducted above ~100°C.

Figure 6 shows the FTIR spectra of the films before and after annealing at 80°C for 1 h. By comparing these spectra, a slight variation is only observed in the absorption bands in the wavenumber range of 620–730 cm^{-1} . Tadokoro et al.¹⁸ pointed out that the band splittings and additional weak bands can occur in PVDF films because of the effect of disordered structures consisting of slightly deflected chains. The slight increase in magnitude of

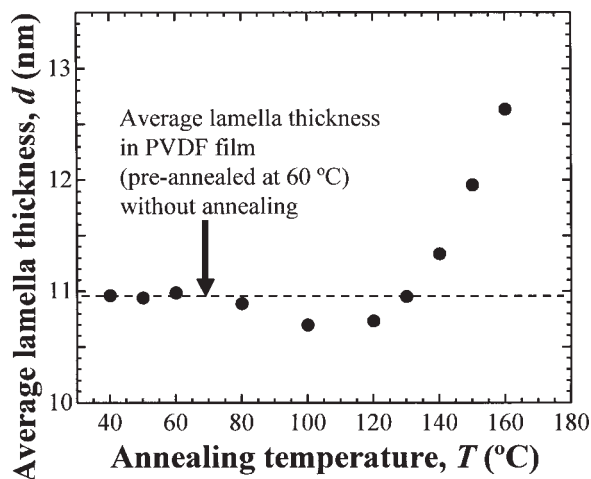


Figure 5 Variation in the average lamella thickness in the PVDF films preannealed at 60°C after annealing at 40–160°C for 1 h.

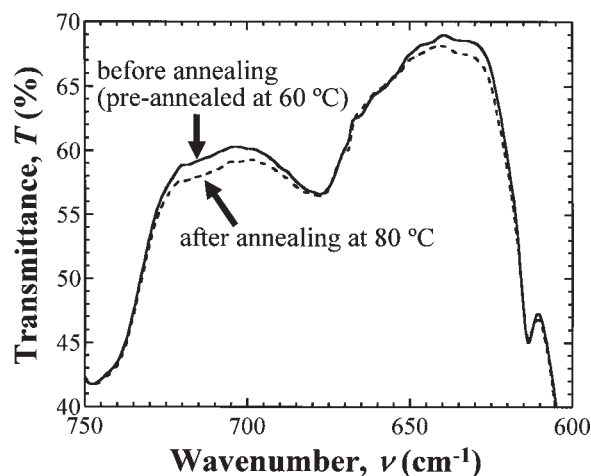


Figure 6 FTIR spectra of the PVDF films preannealed at 60°C before and after annealing at 80°C for 1 h.

the bands due to annealing at 80°C (shown in Fig. 6) is supposed to relate to the development of some disordered structures. By contrast, the magnitude of some bands that are attributed to disorders in molecular conformation becomes large significantly after annealing above 100°C, as shown in Figure 7. Therefore, some kind of disordered structures are considered to be developed significantly during thickening of the lamella crystals.

The SAXS analysis was also applied to estimate variations in the average lamella thickness due to annealing in films preannealed at 100 and 120°C. Figure 8 shows the relationship between annealing temperature and average lamella thickness in these films. Lamella thickening is also observed in these films. Interestingly, the average lamella thickness seems to be principally determined by the annealing temperature, regardless of the preannealing temperature, when the annealing is conducted above the preannealing temperatures.

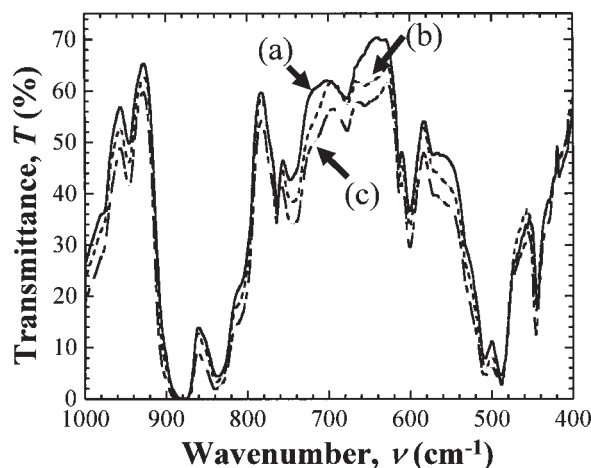


Figure 7 FTIR spectra of the PVDF films preannealed at 60°C after annealing at (a) 100, (b) 120, and (c) 150°C for 1 h.

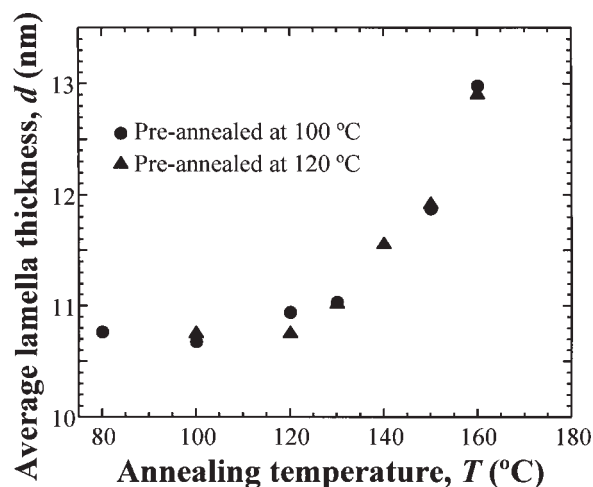


Figure 8 Variations in the average lamella thickness in the PVDF films preannealed at 100 and 120°C after annealing at 80–160°C for 1 h.

Polymeric-structural features of the PVDF film after annealing above the melting temperature

When the PVDF films are annealed at elevated temperatures above the melting temperature (160–170°C), the crystallinity is significantly decreased because melting and recrystallization is promoted during the annealing and subsequent cooling processes. Figure 9 shows the FTIR spectrum of a film annealed at 200°C for 1 h. The specimen was rapidly cooled in air after the annealing process. The spectrum indicates that the β -form crystals are formed as well as the α -form crystals during the recrystallization. This result agrees with the result of WAXD analysis reported in a previous article.¹⁰ The FTIR

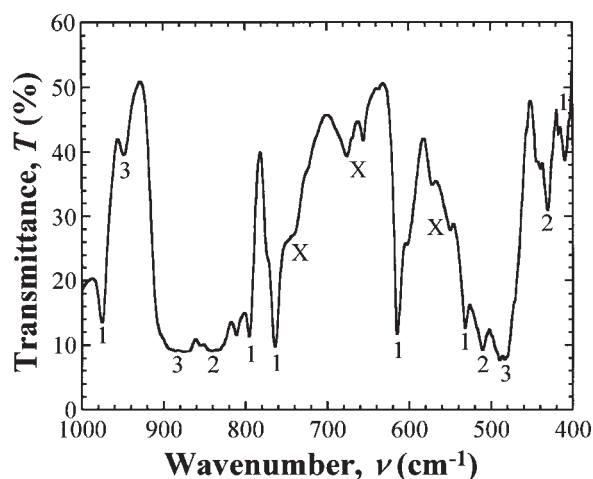


Figure 9 FTIR spectrum of PVDF film preannealed at 60°C after annealing at 200°C for 1 h. The film was rapidly cooled in air after the annealing process. The absorption bands are categorized into four groups; 1: group 1 (α -form), 2: group 2 (β -form), 3: group 3 (both forms), X: disordered structures.

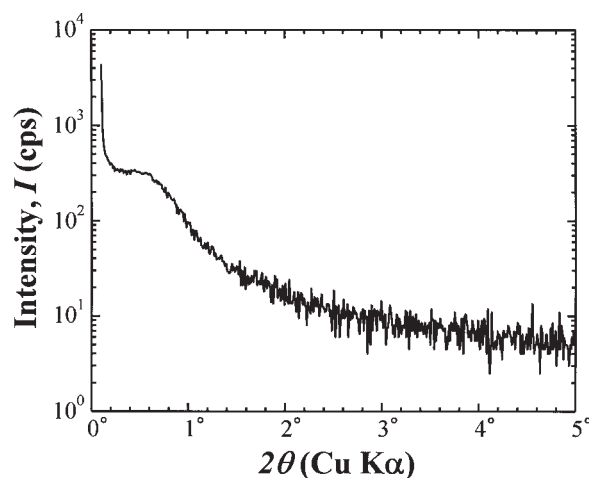


Figure 10 SAXS profile of PVDF film preannealed at 60°C after annealing at 200°C for 1 h.

spectrum suggests that some disordered structures are also formed during the recrystallization.

Figure 10 shows the SAXS profile of a film annealed at 200°C for 1 h. A broad peak, which suggests the existence of a long-range periodic structure, is apparently observed at 0.4–0.7° in 2θ . If the stacked lamellar structure (which is formed because of mechanical stretching during the fabrication process of the films) disappeared completely in the melting state, no long-range periodic structures are formed after solidification. Therefore, this SAXS profile suggests that the nuclei originating from the lamella crystals existed before melting were formed in the melting state.

Discussion regarding annealing mechanisms of the PVDF films

The present authors have previously reported various nonequilibrium phenomena that are observed in PVDF films during the annealing process.¹⁰ The high-ordered structure (such as stacked lamellar structure) that was formed during the fabrication process is considered to be the critical factor that controls these phenomena. For example, the β -phase of PVDF is believed to thermodynamically transform to the α -phase during the annealing process.³ However, a phase transformation to the α -phase had never been observed in the present PVDF films. The experimental results of SAXS (Figs. 5 and 8) and WAXD (Fig. 3) indicated thinning and thickening in the lamella thickness because of annealing although the crystallinity of the β -form crystals decreases monotonically with increasing annealing temperature. Because the motion of the polymer chains that exhibit the topological nature^{11–15} should be restricted because of the existence of the high-order

structures, then phase transformation is suppressed in these films.

By combining the information from WAXD with that from SAXS, it is considered that there are two kinds of relaxation mechanisms during annealing of the PVDF films. Relaxation originating from the formation of disorder structures, such as deflection of polymer chains, is likely to occur in the temperature range between the preannealing temperature and $\sim 100^\circ\text{C}$. As a result of FTIR spectroscopy (Fig. 6), some disordered structures were suggested to be developed during annealing at 80°C although the molecular conformation in regular crystalline regions was not varied. In this case, the disorder structures that intrinsically exist in the PVDF film are likely to predominantly play an important role in this relaxation mechanism. Since the films were mechanically stretched during the fabrication process to stabilize the β -phase of PVDF, residual stress would have been introduced into the films. The residual stress can be partly released because of the aforementioned relaxation mechanism during the annealing process, and hence the average lamella thickness can be decreased by this relaxation mechanism. In this case, the piezoelectric coefficients of the films decrease with decrease in crystallinity accompanied by the lamella thinning.

By contrast, the thickening of the lamellae occurs in the temperature range above $\sim 100^\circ\text{C}$. The thickening is considered to be due to Ostwald's ripening accompanied by interlamella diffusion (sliding diffusion) of the polymer chains.^{13–14}

The previous article¹⁰ discussed the relationship between the β -phase content and the piezoelectric coefficients of the PVDF film. In the temperature range up to 100 – 120°C , the piezoelectric coefficients decreased in proportion to the β -phase content. However, the ratio of the decrease in the piezoelectric coefficients was apparently large compared with that in the content of the β -phase in the temperature range above 100 – 120°C . In addition, Johnson et al.^{20,21} pointed out that there is an additional relaxation mechanism above $\sim 100^\circ\text{C}$ in PVDF films because the kinetics of the shrinkage and of the decrease in piezoelectricity cannot be characterized by a single activation energy in this temperature range. The additional relaxation mechanism that was predicted by Johnson et al.^{20,21} is attributed to the thickening of the lamellar crystals. When sliding diffusion of the polymer chains occurs, which thickens the lamellar crystals, many defects²² and disorders should be introduced into the crystalline regions, resulting in a decrease in the magnitude of polarization in the crystallites. In fact, FTIR spectra (Fig. 7) show the magnitude of absorption bands that relate to the disordered structures significantly increases accompanied by the thickening of the lamellar crys-

als. The disordered structures formed during the lamella thickening are likely to cause the additional decrease in piezoelectricity.

Figure 8 shows how the average lamella thickness in the PVDF films is determined by the highest annealing temperature, regardless of the thermal history of the films. During the annealing process, the lamellar crystals in the films adopt a meta-stable state, which is determined by the annealing temperature. The free energy of the meta-stable states is likely to be lowered with increasing annealing temperature because the meta-stable crystals can exist stably in the temperature range below the annealing temperature after the annealing process.¹⁰ In other words, the lamella thickening is an irreversible process, in addition to the development of disordered structures below $\sim 100^\circ\text{C}$. This irreversible annealing effect is important for controlling the thermal stability of the PVDF films.¹⁰

The effect of the high-order structure extends to the melting and recrystallization behavior of the PVDF films. The SAXS profile indicates the existence of a long-range periodic structure in the film after annealing at 200°C as shown in Figure 10. This experimental result suggests that some localized ordered structures¹⁵ originating from the stacked lamellar structure in the films before annealing remained meta-stably in the melting state, even at 200°C . Because these localized ordered structures can act as nuclei for recrystallization, a long-range periodic structure is considered to be formed in the film after solidification, as shown in Figure 10. In addition, the β -phase (which is not usually formed during the recrystallization process) was detected in the film by WAXD¹⁰ and FTIR (Fig. 9) after annealing at 200°C . The formation of the β -phase is also believed to be related to the localized ordered structures that exist meta-stably in the melting state during the annealing process.

The polymeric structures of PVDF films can be widely controlled, depending on the exact fabrication conditions.^{6–9,23} Because the polymeric structures in these films significantly influence the annealing behavior (as discussed in this section), the thermal stability should be examined with reference to the polymeric-structural features (including high-order structures and disorders in the crystalline region) of the films formed during the fabrication process.

CONCLUSIONS

Variations in the polymeric structures in ferroelectric PVDF films due to annealing are discussed in this article based on analyses of SAXS profiles and FTIR spectra. The main results obtained in the present work are summarized as follows:

1. A stacked lamellar structure is formed perpendicular to the drawing direction in uniaxially drawn PVDF films during the fabrication process. In addition, some disordered structures in molecular conformation such as head-to-head or tail-to-tail linkages can be formed in the films during the process.
2. The lamella thickness slightly decreases simultaneously with the crystal relaxation due to annealing in the temperature range between the preannealed temperature and $\sim 100^\circ\text{C}$. By contrast, significant lamella thickening accompanied by sliding diffusion of the polymer chains occurs during annealing above $\sim 100^\circ\text{C}$. The disordered structures are developed during the thinning and thickening of the lamellar crystals.
3. The lamella thickness that is achieved after annealing is mostly determined by the highest annealing temperature, regardless of the thermal history of the films.
4. A long-range periodic structure can be formed in the films during the annealing process (including melting and recrystallization processes) above the melting temperature of PVDF.

The authors thank Mr. S. Tsuda (Tokyo Sensor Co., Ltd.), Messrs T. Kawasaki, T. Rokuhara, Y. Bando, Y. Kawahito, Y. Yoshino (Togawa Rubber Co., Ltd.), and Mr. T. Hondo (Vstone Co., Ltd.) for many helpful suggestions. The authors also acknowledge Professor T. Suzuki and Mr. T. Tanaka (the Materials Analysis Center, ISIR, Osaka University) for their support when making use of the SAXS, WAXD, and FTIR equipments.

References

1. Cheng, Z.; Zhang, Q. *MRS Bull* 2008, 33, 183.
2. Murayama, N.; Nakamura, K.; Obara, H.; Segawa, M. *Ultrasonic* 1976, 14, 15.
3. Kochervinskii, V. V. *Crystallogr Rep* 2003, 48, 649.
4. Davis, G. T.; McKinney, J. E.; Broadhurst, M. G.; Roth, S. C. *J Appl Phys* 1978, 49, 4998.
5. Broadhurst, M. G.; Davis, G. T. *Ferroelectrics* 1984, 60, 3.
6. Hikosaka, M.; Sakurai, K.; Ohigashi, H.; Koizumi, T. *Jpn J Appl Phys* 1993, 32, 2780.
7. Omote, K.; Ohigashi, H.; Koga, K. *J Appl Phys* 1997, 81, 2760.
8. Koga, K.; Nakano, N.; Hattori, T.; Ohigashi, H. *J Appl Phys* 1990, 67, 965.
9. Li, Y.; Kaito, A.; Horiuchi, S. *Macromolecules* 2004, 37, 2119.
10. Inoue, M.; Tada, Y.; Sugauma, K.; Ishiguro, H. *Polymer Degradation and Stability* 2007, 92, 1833.
11. Hikosaka, M. *Polymer* 1987, 28, 1257.
12. Hikosaka, M. *Polymer* 1990, 31, 458.
13. Hikosaka, M.; Rastogi, S.; Keller, A.; Kawabata, H. *J Macromol Sci Pt B Physics* 1992, 31, 87.
14. Hikosaka, M. *Kobunshi* 1993, 42, 500. (in Japanese).
15. Hikosaka, M. *Oyo Buturi* 1994, 63, 692. (in Japanese).
16. Fischer, E. W.; Goddar, H.; Schmidt, G. F. *Makromol Chem* 1968, 118, 144. (in German).
17. Enomoto, S.; Kawai, Y.; Sugita, M. *J Polym Sci A-2* 1968, 6, 861.
18. Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* 1975, 8, 158.
19. Mohammadi, B.; Yousefi, A. A.; Bellah, S. M. *Polymer Testing* 2007, 26, 42.
20. Blyler, L. L. Jr.; Johnson, G. E.; Hylton, M. *Ferroelectrics* 1980, 28, 303.
21. Johnson, G. E.; Blyler, L. L. Jr.; Crane, G. R.; Gieniewski, C. *Ferroelectrics* 1981, 32, 43.
22. Wada, Y. *Kobunshi no Kotaibussei; Baifukan: Tokyo*, 1971, p. 94. (in Japanese).
23. Nakamura, K.; Nagai, M.; Kanamoto, T.; Takahashi, Y.; Furukawa, T. *J Polym Sci Pt B Polymer Physics* 2001, 39, 1371.