ORIGINAL ARTICLE

The optical transparency and structural change of quenched poly(vinylidene fluoride) caused by cold-drawing

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We found that poly(vinylidene fluoride) (PVDF) film quenched in ice-water became transparent by cold-drawing, whereas PVDF that was slowly cooled on a hot plate became opaque. The transmittance of the quenched PVDF measured by ultraviolet–visible spectroscopy increased by up to 30% in the lower wavelength range (200–600 nm), which indicated increased transparency. A four-point small-angle X-ray scattering (SAXS) pattern was observed at a strain of 18% just after the yield point without the change of the lamellar periodic distance, suggesting the rotation of the crystalline lamellae without fragmentation. This specific deformation behavior prevented the formation of nanometer-sized voids, which decreased the transparency of the slowly cooled PVDF. Interestingly, the integrated SAXS intensity from the lamellar crystal decreased as the strain increased. Therefore, the decrease in the density difference between the lamellar crystal and the lamellar amorphous phases might increase the transmittance of the quenched PVDF in the lower wavelength range.

Polymer Journal (2013) 45, 1033–1040; doi:10.1038/pj.2013.26; published online 13 March 2013

Keywords: cold-drawing; Hv light scattering; poly(vinylidene fluoride); quench; SAXS

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is an excellent functional polymer that exhibits high chemical resistance, high thermal stability and ferroelectricity. In addition, owing to its good processability, PVDF has been one of the most commonly used fluorinated polymers in daily life and industry. Recently, the preparation of the transparent fluorinated polymer film has been extensively investigated to extend its applicability by using various methods, such as blending with miscible polymers^{1,2} or nanoparticles,³ synthesizing non-crystalline structures,^{4–6} casting the solution followed by pressing^{7,8} and drawing the fluorinated polymers at high temperature.^{9,10} However, to prepare transparent single-component PVDF films, energy-consuming processes at high pressure^{7,8} or high temperature¹⁰ were required.

The deformation of the crystalline polymer is a facile physical processing method used to control the crystalline structures and improve the polymer properties. During the deformation process, the hierarchical structure of the polymer changes. The nanometer-sized lamellar crystals orient and the micrometer-sized spherulites transform into the fibril and are aligned in the drawing direction.^{11–16} However, in case of cavitating polymers, voids appear between the sheared and tilted lamellar crystals near the yield point, in addition to the structural development of the crystal.^{17–23} Because a large refractive index difference exists between the polymers and the voids, the light is strongly scattered. As a result, the deformed

polymer becomes white, which is often disadvantageous for polymeric materials. However, crystalline polymers can be deformed without cavitation by drawing at high temperatures^{7,8,24} or by drawing the quenched polymer.^{21–23,25} Then, the plastic deformation occurs readily owing to the enhanced mobility of the polymer chain, and no cavitation is observed.

In this study, we describe a facile method to prepare transparent PVDF film with good transmittance over a wide wavelength range (from 200 to 900 nm) by means of cold drawing. To avoid the voiding of PVDF, we used quenched PVDF films. The change in the transparency caused by the drawing, whether the transmittance increases or decreases depending on the light wavelength, was examined using ultraviolet–visible (UV–vis) spectroscopy. In addition, the structure–property relationship during the drawing process was investigated using Hv light scattering, small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements. The results from the cold-drawing were discussed and compared with the deformation behavior of PVDF films that were slowly cooled on a hot plate; in these films, the void appeared, and the film became opaque during the drawing process.

EXPERIMENTAL PROCEDURE

PVDF ($M_w = 2.2 \times 10^5$, $M_w/M_n = 2.2$, KF1000) was supplied by Kureha Chemical Industry Co., Ltd. (Tokyo, Japan), and used without further

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Received 17 December 2012; revised 16 January 2013; accepted 17 January 2013; published online 13 March 2013

purification. PVDF was melted at 200 °C for 5 min and pressed to a film thickness of 100 μm . The PVDF film was melted at 200 °C for 3 min and then rapidly placed on a hot plate at 30 °C or dipped into ice water at 0 °C. The PVDF crystallized on the hot plate at 30 °C was designated as H30, and the PVDF crystallized in ice water at 0 °C was designated as W0.

For the Hv light scattering measurements, a polarized He–Ne laser with a wavelength of 632.8 nm was applied vertically to the film specimen. We employed an Hv geometry in which the optical axis of the analyzer was perpendicular to that of the polarizer.²⁶ The scattered light passed through the analyzer and then onto a highly sensitive charge-coupled device camera with 800 $\times$ 600 pixels (pco.1600; Tokyo Instruments Inc., Tokyo, Japan). The input data from the charge-coupled device camera were stored in a personal computer for further analysis.

The tensile-deformation measurement was performed at 25 °C at a cross-head speed of 10 mm min^{−1} using the STROGRAPH 05D (Toyo Seiki Seisaku-sho Ltd., Tokyo, Japan). A rectangular specimen with a dimension of 10 $\times$ 30 mm² was cut from the PVDF film for the measurement. The specimen was drawn up to an aimed strain and was kept for 1 h to relax the stress and then used for UV–vis spectroscopy, SAXS and WAXD measurements.

The transmittance of the deformed PVDF film as a function of the light wavelength was investigated using UV–vis spectroscopy (V-550; Jasco, Hachioji, Japan). The wavelength range was from 200 to 900 nm, and the wavelength scan speed was 400 nm min^{−1}. The accuracy of the equipment with regard to transmittance was $\pm 0.3\%$.

WAXD and SAXS measurements were performed using the NANO-Viewer system (Rigaku Co., Tokyo, Japan). Cu–K α radiation (46 kV, 60 mA) was generated and collimated by a confocal max-flux mirror system. The wavelength was 0.154 nm. The sample-to-detector distance was 15 mm for WAXD and 700 mm for SAXS. An imaging plate (IP) (BAS-SR 127; Fujifilm Corp., Tokyo, Japan) was used as a two-dimensional detector, and the IP reading device (R-Axis Ds3; Rigaku Co.) was used to transform the obtained image into text data. The exposure times were 15 min for WAXD and 2–16 h for SAXS. The scattering intensities were corrected with respect to the exposure time, the sample thickness and the transmittance.

Differential scanning calorimetry measurements were conducted using a DSC8230 (Rigaku Co.) at ambient pressure conditions. The center of the deformed specimen was cut and used for the measurements. The differential scanning calorimetry scans were performed at a heating rate of 10 °C min^{−1}.

RESULTS AND DISCUSSION

The superstructures of the prepared PVDFs before drawing were investigated by two-dimensional Hv light scattering. H30 exhibited a four-leaf-clover-type scattering pattern (Figure 1a), which is typical of the spherulite superstructure and is usually observed for crystallized PVDF.^{27,28} By contrast, W0 showed a rod-like scattering pattern (Figure 1b). This result indicates that the superstructure of W0 is a randomly oriented rod-like structure, in which the lamellae are stacked, without the formation of a higher-order structure.^{29–31} Notably, the angle between the long axis of the lamellar stack and

Figure 1 The Hv light scattering patterns of (a) poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30 °C (H30) and (b) PVDF crystallized in ice water at 0 °C (W0).

the normal direction of the lamellar surface was 45°. During quenching, the PVDF chain did not have enough time for crystallization, and the crystalline chain could not pack into the more stable structure. The arrangement of the lamellar stack toward regularly ordered superstructures, such as the spherulite, was also prevented.

Figure 2 shows the stress–strain curves of H30 and W0. The yield strains of both PVDFs were commonly approximately 11.5%. The yield stress and plateau stress of W0 were 10 MPa lower than those of H30, although the two PVDFs have comparable crystallinity (Table 1). As revealed by the Hv light scattering measurement, W0 has a randomly oriented rod-like superstructure, whereas H30 has a rigid spherulite superstructure. Therefore, the structure of W0 could be easily deformed by an applied force. The stress hardening occurs near 400% due to the entropic stress of the elongated polymer chain. At this point, the deformed W0 started to become opaque. Therefore, we conducted the following experiments up to a strain of 300%.

Figure 3 shows the photographs of the prepared PVDFs before and after cold-drawing at a strain of 300%. Before drawing, both of the PVDFs were translucent. However, H30 became opaque as a result of drawing (Figure 3, left). This reduction in the transparency of the crystallized PVDF caused by drawing was reported previously^{18,32–34} and is often attributed to the void formation near the yield point. By contrast, the transparency of W0 did not decrease but rather increased because of cold-drawing (Figure 3, right). This increase in transparency caused by cold-drawing is the opposite result to that of H30.

To understand in detail how the change in the transparency depends on the wavelength of the light, UV–vis spectroscopy was performed on both of the deformed PVDFs. As the strain increased, the transmittance of H30 decreased substantially over the entire

Figure 2 The stress–strain curves of poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30 °C (H30) and PVDF crystallized in ice water at 0 °C (W0).

Table 1 Crystallinities (%) of the PVDF films at various strains obtained by DSC measurements

Sample	Strain (%)			
	0	100	200	300
H30	45.9	53.6	54.4	59.3
W0	42.9	49.2	53.6	56.7

Abbreviations: DSC, differential scanning calorimetry; H30, PVDF crystallized on the hot plate at 30 °C; PVDF, poly(vinylidene fluoride); W0, PVDF crystallized in ice water at 0 °C (W0).

Figure 3 Photographs of poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30 °C (H30) and PVDF crystallized in ice water at 0 °C (W0) before and after drawing, up to a strain of 300%.

Figure 4 The transmittance as a function of light wavelength for (a) poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30 °C (H30) and (b) PVDF crystallized in ice water at 0 °C (W0) under various strains, as measured by ultraviolet–visible (UV–vis) spectroscopy. The data are normalized to the thickness at 100 μm .

measured wavelength range (Figure 4a). However, the transmittance of W0 increased by up to 30% in the lower wavelength range (200–600 nm), whereas the transmittance decreased slightly in the higher wavelength range (600–900 nm; see Figure 4b). Therefore, the increase in the transparency of W0 that was visually observed can be ascribed to the increase in the transmittance in the wavelength range between 380 and 600 nm. The deformed W0 films exhibit a high transmittance of approximately 40% at 200 nm, and the transmittance over the entire wavelength range (300–900 nm) is more than 80%. Considering that the transmittances of commodity polymers such as poly(methyl methacrylate) and polycarbonate drop rapidly to zero at approximately 300 nm,³⁵ the deformed film of the quenched PVDF exhibited good transparency over the entire wavelength range.

Here, the correlation between the change in the transmittance and the change in the structure is discussed based on the SAXS result. Figure 5 shows the two-dimensional SAXS patterns of H30 as a function of the strain. At a strain of 0%, the SAXS pattern is isotropic. While the lamellar stacks were radially arranged in the spherulite superstructure, the orientation of the lamellar crystal was random on average in the irradiated X-ray area. At a strain of 18%, the drawn film became opaque, and a strong streak appeared in the meridional direction. This strong streak originated from the formation of the void perpendicular to the draw direction.^{17,18,23} Although the scattering pattern from the lamellar crystal could not be distinguished because of the overlap with a strong and wide streak, the void formation suggests intralamellar shear and, hence, the fragmentation of the lamellar crystal. Above a strain of 100%, the direction of the streak became equatorial. During the fibrillation of the spherulite, the lamellar crystals were well arranged in the draw direction; then, the voids became elongated in the draw direction.

As the strain was increased above 100%, the intensity of the streak increased. To clarify this finding, we estimated the increase in the scattering intensity of H30 using the invariant, Q_{H30} , in the two-dimensional pattern, which is given by³⁶

$$Q_{\text{H30}} = \int_S I(\mathbf{q}) \cdot d\mathbf{q} \quad (1)$$

where S is the detector area, $I(\mathbf{q})$ is the scattering intensity at $\mathbf{q}$ and $\mathbf{q}$ is the scattering vector; $d\mathbf{q}$ is the volume element in two-dimensional reciprocal space and is defined by $d\mathbf{q} = q \cdot dq \cdot d\phi$, where q is the magnitude of the scattering vector defined by $q = 4\pi/\lambda \sin \theta$ at scattering angle θ ; λ is the wavelength of the X-ray (0.154 nm); and ϕ is the azimuthal angle. As the strain increased to 300%, Q_{H30} increased by up to 45% from 1.57×10^{-4} to 2.28×10^{-4} (Figure 6a). The increase in the scattering intensity can be ascribed to the increase in the volume fraction of the void, which is the product of the volume of the void and the number density of the void.³⁶ Therefore, to reveal the structural change of the void in the deformed PVDF, we estimated both the length of the void in the drawing direction and the cross-sectional radius of the void perpendicular to the drawing direction. The analysis of the length of the void was performed using the intensity distribution of the equatorial streak in the two-dimensional SAXS pattern via the so-called Ruland's method.^{37–39} The azimuthal intensity distributions at different scattering angles were fitted with Lorentz functions, which produced the following equation:

$$B_{\text{obs}} B = \frac{2\pi}{L \times q} + B_{\phi} (\text{Cauchy} - \text{Cauchy}) \quad (2)$$

where B_{obs} is the integral width of the azimuthal intensity distribution, L is the effective length of the void in the draw

Figure 5 The strain dependence of the two-dimensional SAXS pattern for poly(vinylidene fluoride) crystallized on the hot plate at 30 °C (H30).

direction and B_ϕ is the misorientation width of the void. We can obtain L from the slope of B_{obs} vs $1/q$. Figure 6b shows the strain dependence of the obtained void length, L , of H30 on the left axis. Because the obtained L values were approximately 70 nm in length, the voids were nanometer-sized. Although L monotonically increased as the strain increased, the increase rate was small.

The cross-sectional radius of the void perpendicular to the draw direction was qualitatively estimated using the Guinier approximation on the SAXS profile in the equatorial direction.^{22,40} The approximation is applied in the low q range and is represented by

$$I(q) \approx \exp\left(-\frac{q^2 R^2}{5}\right) \quad (3)$$

where R is the circular cross-sectional radius of the void. Figure 6b shows the decrease in R with increasing strain on the right axis. This result suggests that the elongation of the void in the draw direction accompanies the shrinkage of the cross-section.

Finally, by assuming the void to be of ellipsoidal shape, the volume of the void, V , was estimated using the following equation:

$$V = \frac{4}{3} \pi R^2 \left(\frac{L}{2}\right) \quad (4)$$

Figure 6c shows that V did not change or slightly decreased as the strain increased. This result is due to the shrinkage of the deformed PVDF upon unloading, which was clearly visually observed, even at a strain of 100%. Therefore, the structural change of the void does not explain the further decrease in the transmittance as the strain increased above a strain of 100%. As a result, the increase in the volume fraction of the void can be ascribed to an increase in the number density of the voids rather than to an increase in the volume of the voids. The increase in the volume fraction of the voids further increased the scattering intensity and decreased the transmittance.

It should be noted that the nanometer-sized voids are not primarily responsible for the whitening of the deformed polymer because they are sufficiently shorter than the wavelength of the visible light.

However, because the formation of the nanometer-sized voids is accompanied by the formation of micrometer-sized voids^{20,21,24} and because a large refractive index difference exists between the nanometer-sized voids and the surrounding lamellar clusters (which have dimensions of several hundred nanometers),⁴¹ the SAXS result with respect to the nanometer-sized voids can be an important clue regarding the change in the transparency.

Next, the correlation between the change in the transmittance and the change in the structure of W0 was investigated using two-dimensional SAXS results (Figure 7). As the strain increased above the yield point, moderately strong scattering appeared in the center of the SAXS pattern, and the strong streak from the nanometer-sized void was not observed. Because the larger scattering object appeared in the center region, this specific pattern originates from the formation of large voids or a large inhomogeneous structure, which might cause the subtle decrease in the transmittance of W0 in the wavelength range above 600 nm.

At a strain of 0%, the SAXS pattern was isotropic, and the lamellar stacks were randomly oriented. At a strain of 18% just after the yield point, the isotropic circular pattern changed to the four-point SAXS pattern at an azimuthal angle of 45°, suggesting that the lamellar crystals were oriented in the draw direction. After further drawing, the four-point pattern shifted toward the meridional direction, and the azimuthal angle decreased to 24°, which indicates the enhanced orientation of the lamellar crystal in the draw direction. These structural developments are discussed in detail by analyzing the one-dimensional SAXS curve as follows.

Figure 8 shows the Lorentz-corrected one-dimensional SAXS curves of (a) H30 in the meridional direction and (b) W0 in the peak direction. The scattering intensity was multiplied by the square of q for the Lorentz correction.^{42,43} By Lorentz-correcting the data, the scattering peak of H30 from the periodic distance of the lamellar crystal could be distinguished above a strain of 100%, although it was overlapped by the strong streak from the nanometer-sized void. Before drawing, the peak position was 0.60 nm^{-1} , and the periodic distance was estimated using Bragg's equation ($d = 2\pi/q_{\text{peak}}$) to be

Figure 6 The strain dependences of (a) the invariant of poly(vinylidene fluoride) crystallized on the hot plate at 30 °C (H30), (b) the length of the void, L (left axis), and the cross-sectional radius, R (right axis), and (c) the volume of the void, V , a.u., arbitrary unit.

10.4 nm. At a strain of 100%, although the strong upturns from the voids appeared in the lower wavenumber range, subtle peaks could be observed at approximately 0.89 nm^{-1} . This result suggests that the lamellar crystals were fragmented by cold-drawing and that the increased number of lamellar crystals decreased the periodic distance to 7.1 nm.

By contrast, in the case of W0, the upturn from the large voids or the inhomogeneous structures was depressed, and the peaks from the lamellar crystals were clearly observed, as shown in Figure 8b. At a strain of 0%, the peak position was 0.76 nm^{-1} . Therefore, the lamellar crystals with the shorter periodic distance of 8.3 nm were obtained by quenching in ice water. At a strain of 18%, just after the yield point, the four-point SAXS pattern suggesting the orientation of lamellar crystal was observed, as shown in Figure 7. However, the peak position did not change by drawing up to 18%. Therefore, the lamellar crystal and the higher-order lamellar stack were rotated in the draw direction without fragmentation of the lamellar crystals. Because W0 could be easily deformed with less force, as shown in Figure 2, the stress concentration on the amorphous region would be

suppressed. This specific deformation of the lamellar crystal may lead to the rotation of the lamellar crystal in the drawing direction without the formation of the nanometer-sized void. Above a strain of 100%, the peak shifted toward the higher q , suggesting the fragmentation of the lamellar crystals by further drawing. Because the strong streak did not appear in the two-dimensional SAXS pattern after the alignment of the lamellar crystals in the draw direction, the formation of the nanometer-sized void was prevented during fragmentation.

Furthermore, the density difference between the lamellar crystal and the lamellar amorphous phases of W0 was estimated using the invariant of the lamellar crystal. The Lorentz-corrected scattering curve can be divided into two parts, the lamellar peak and the higher-order inhomogeneity, as follows:

$$I(q) = I_{\text{peak}}(q) + I_{\text{power}}(q) \quad (5)$$

where $I_{\text{peak}}(q)$ is the scattering from the stacked lamellar crystal and $I_{\text{power}}(q)$ is the scattering from the higher-order inhomogeneity. In this study, $I_{\text{peak}}(q)$ was represented by the lognormal function to fit the scattering peak, $I_{\text{peak}}(q) \sim 1/(q\sigma) \cdot \exp(-(\ln(q)-\mu)^2/2\sigma^2)$, where μ and σ are the mean and the standard deviation of the natural logarithm of the variable, respectively. $I_{\text{power}}(q)$ was represented by the power-law function, $I_{\text{power}}(q) \sim q^\alpha$, where α is the exponent of -0.64 . The solid curves generated by equation (5) showed good fits to the scattering curves (Figure 8b).

The invariant of the lamellar crystal of W0 was calculated by integrating the Lorentz-corrected scattering intensity, $I_{\text{peak}}(q)$, in the overall q range.³⁶ By assuming a two-phase system of the lamellar crystal and the lamellar amorphous phase, the invariant, Q , is expressed using the following equation:

$$Q = K \cdot \phi_c \cdot (1 - \phi_c) \cdot \Delta\rho^2 \quad (6)$$

where K is the constant illuminated volume of the X-ray, ϕ_c is the volume fraction of the crystalline region and $\Delta\rho$ is the electron density difference between the lamellar crystal and the lamellar amorphous phases. Figure 9a shows the invariant, Q , as a function of the strain. As the strain increased, Q monotonically decreased. Thus, $\Delta\rho^2$ can be described by

$$\Delta\rho^2 = \frac{Q}{K \cdot \phi_c \cdot (1 - \phi_c)} \quad (7)$$

ϕ_c was calculated using the following equation:⁴⁴

$$\phi_c = \frac{\rho_a \cdot X_c}{(\rho_a - \rho_c)X_c + \rho_c} \quad (8)$$

X_c is the degree of the crystallinity, which is shown in Table 1. ρ_a and ρ_c are the densities of the amorphous region (1.667 g cm^{-3}) and the crystalline regions before (α phase, 1.925 g cm^{-3}) and after (β phase, 1.973 g cm^{-3}) drawing, respectively.⁴⁵ Figure 9b also shows the monotonic decrease in $\Delta\rho^2$ as the strain increased. This result suggests the density difference between the lamellar crystal and the lamellar amorphous phases decreased as the strain increased. The drawn lamellar amorphous phase increased in density because of the alignment of the polymer chain along the draw direction. This reduced scattering intensity caused by the decrease in the density difference is one of the keys to increasing the transmittance in the lower wavelength range.

The orientation of the lamellar crystal and the higher-order lamellar stack of the deformed PVDF were further investigated by WAXD measurements (Figure 10). The anisotropic WAXD patterns were observed, and the scattering peaks indicating the (001) reflections of the c axis appeared in the meridional direction of both of the PVDFs. The orientation degree of the lamellar crystal was

Figure 7 The strain dependence of the two-dimensional small-angle X-ray scattering (SAXS) pattern for poly(vinylidene fluoride) crystallized in ice water at 0°C (WO).

Figure 8 The strain dependences of the Lorentz-corrected one-dimensional small-angle X-ray scattering (SAXS) curves for (a) poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30°C (H30) and (b) PVDF crystallized in ice water at 0°C (WO). Each curve is shifted by a factor of 10ⁿ ($n=1, \dots, 4$) to avoid overlap. The solid curves are fits generated using equation (5). a.u., arbitrary unit.

Figure 9 The strain dependences of (a) the invariant, Q , of the lamellar crystal of poly(vinylidene fluoride) crystallized in ice water at 0°C (WO) and (b) the electron density difference between the lamellar crystal and the lamellar amorphous phases, $\Delta\rho^2$.

Figure 10 The two-dimensional WAXD patterns of drawn poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30 °C (H30) and PVDF crystallized in ice water at 0 °C (W0) at a strain of 300%.

Figure 11 Schematics showing the structural changes of (a) poly(vinylidene fluoride) (PVDF) crystallized on the hot plate at 30 °C (H30) and (b) PVDF crystallized in ice water at 0 °C (W0) during the drawing process.

estimated using the Hermans orientation parameter, f_c .³⁶ The f_c values were high: 0.86 for H30 and 0.87 for W0. This WAXD result suggests that the normal direction of the lamellar crystals was aligned in the draw direction. Therefore, the origin of the four-point SAXS pattern is attributed to the tilting of the long axis of the lamellar stack toward the draw direction rather than to the tilting of the lamellar crystal toward the draw direction. The schematics of the structural changes of H30 and W0 during the drawing process are shown in Figure 11.

CONCLUSIONS

The optical transparency and structural change of the quenched PVDF film caused by cold-drawing were investigated using Hv light scattering, tensile deformation, UV-vis spectroscopy, SAXS and WAXD. The transmittance in the lower wavelength range (200–600 nm) increased by up to 30%, which increased the transparency of the quenched PVDF film, whereas the transmittance in the

higher wavelength range (600–900 nm) subtly decreased. The SAXS measurements revealed that a large inhomogeneous structure appeared beyond the yield point. This structure would decrease the transmittance at the higher wavelength. However, a four-point SAXS pattern was observed at a strain of 18%, just after the yield point, without a change in the lamellar periodic distance, suggesting the rotation of the crystalline lamellae without fragmentation at the yield point. This specific deformation behavior prevented the formation of nanometer-sized voids, which decreased the transparency of the PVDF that was slowly cooled on the hot plate. Interestingly, the integrated SAXS intensity from the lamellar crystal of the quenched PVDF decreased as the strain increased. Therefore, the decrease in the density difference between the lamellar crystal and the lamellar amorphous phases increased the transmittance in the lower wavelength region.

ACKNOWLEDGEMENTS

This work was partially supported by the Japan Society for the Promotion of Science (Grant-in-Aid for Young Scientists (B), No. 24750214).

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