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Butterfly patterns in crystalline polymers under uniaxial stretch

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We investigate the density fluctuations in crystalline polymers under uniaxial stretch in the order of submicrons to microns with two-dimensional ultrasmall-angle x-ray scattering. Before uniaxial stretch, we found isotropic density fluctuations obeying the mass fractal with the fractal dimension 2.6. After uniaxial stretch, the isotropic scattering pattern was transformed into the butterfly pattern. The butterfly pattern is caused by the stress-induced density fluctuations and the heterogeneous deformation associating with the spatial heterogeneity of stress field due to the distribution of crystalline and amorphous regions.

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I. INTRODUCTION

It is well known that the scattering patterns of swollen polymer gels under stretched uniaxially exhibit the so-called "butterfly pattern" [1,2]. According to theoretical studies [3–7], we can observe "abnormal" butterfly patterns with an increase of the scattered intensity in the direction parallel to the stretch direction in the case of heterogeneous swollen gels. Experimentally, abnormal butterfly patterns are observed in swollen gels since the heterogeneity of cross-linking points is inherent to chemical gels [3]. Abnormal butterfly patterns have also been observed in various systems such as elongated polymer networks swollen by short chains [8], semidilute polymer solutions [9] and polymer blends [10] under shear flow, and mixtures of short and long homopolymers under stretch [11]. Among the theories for the mechanism of the appearance of abnormal butterfly patterns for swollen gels, the cluster model proposed by Bastide *et al.* [3] suggested that the origin of the butterfly patterns is the heterogeneity of deformation: more cross-linked regions are less deformed than less cross-linked regions. The heterogeneity of deformation is thus caused by spatial heterogeneity of dynamical properties. On the other hand, as for the butterfly patterns of semidilute polymer solutions and polymer blends under shear flow, Doi and Onuki (DO) considered the coupling between stress and diffusion caused by the difference in mechanical properties between constituent components in the systems and formulated the time-dependent-Ginzburg-Landau–type dynamical equation which incorporates the term of the gradient of stress field [12]. The computer simulation [13–15] with DO theory for semidilute solutions shows the butterfly patterns in scattering under shear flow.

Crystalline polymers in bulk also have such spatial heterogeneity of stress field. Usually polymers cooled below their melting temperature form spherulite structures. Spherulite structures are filled with branching and splaying fibrils where two-phase structures consisting of lamellar structure of alternating crystalline and amorphous parts are built up. Since the mechanical properties between fibril and nonfibril parts are different, the uniaxial stretch of crystalline polymers results in heterogeneous deformation so that the abnormal butterfly pattern would be observed in the scattered intensity of stretched crystalline polymers. Here, we first report the observation of the butterfly pattern in the scattered intensity of crystalline polymers under uniaxial stretch.

II. EXPERIMENTAL METHOD

We used high density polyethylene (HDPE) film as a crystalline polymer. The weight-averaged molecular weight and the heterogeneity index of HDPE are, respectively, 6.46×10^4 and 7.82. The melt flow index of HDPE is 5.2 g/10 min at 190 °C and 5 Kg load. The pellets of HDPE were placed between stainless-steel plates and molten in a hot-press machine for several minutes at 180 °C and then quickly cooled to room temperature. The sample thickness was 2 mm. The crystalline ratio of the sample was 75.3 wt % determined by DSC. We also measured stress-strain curve at room temperature and we obtained yield stress 2.56×10^7 MPa at the elongation ratio $\varepsilon = 1.08$. The elongation ratio ε is defined by

$$\varepsilon = L/L_0, \tag{1}$$

where L and L_0 are, respectively, the length of the sample after and before stretch. We measured two-dimensional (2D) scattered patterns with the 2D ultrasmall-angle x-ray scattering (USAXS) technique under uniaxial stretch at room temperature. We used long path length (~150 m) and the synchrotron x-ray source so that we can observe 2D scattering patterns at very small wave number q region; $0.005 < q < 0.02\ \mathrm{nm}^{-1}$, where q is defined by

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{2}$$

with λ and θ being wavelength of the incident beam and scattering angle, respectively. In this experiment, we used $\lambda = 0.05$ nm. The detail of the instruments was discussed elsewhere [16]. Since we did not focus the beam at BL20XU, the resolution q range at BL20XU with 150 m path length is comparable to the resolution at BW4, DESY with 12.4 m path length. We measured 2D-USAXS patterns at $\varepsilon = 1.0$ (before stretching) and $\varepsilon = 1.05$. It took 300 s to measure one 2D-USAXS pattern. Small-angle x-ray scattering (SAXS) experiments were also conducted at the

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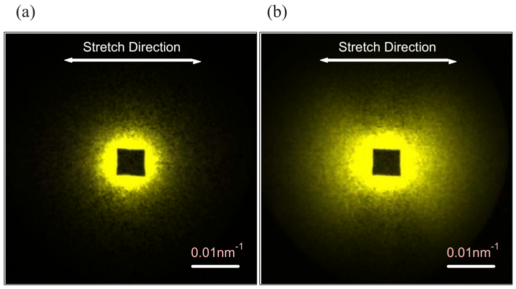

FIG. 1. (Color online) 2D-USAXS pattern of HDPE (a) before uniaxial stretch and (b) after uniaxial stretch at $\varepsilon = 1.05$.

BL45XU, Spring-8 [17] to investigate the changes in lamellar structures associated with uniaxial stretch. Here, x and y axes denote, respectively, the directions parallel and perpendicular to the uniaxial stratch direction. We converted the 2D-SAXS data to absolute intensities by using the scattering intensity of Lupolen while the 2D-USAXS data are relative intensities. For future experiments, we will convert the 2D-USAXS data to absolute intensities by using the scattering intensity of water [18]. An azimuthal φ is defined to be an angle from the x axis. The stress whiting due to crazing did not occur under stretch at $\varepsilon = 1.05$. We observed the sample with optical microscope under stretch at $\varepsilon = 1.05$ and found no voids in the sample. Two-dimensional Vv-light scattering did not show any strong streak except the deformed Vv-light scattering pattern. These facts indicate that the scattered intensity of USAXS does not contain the effects of voids and/or crazing but reflects density fluctuations of polymers.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the 2D-USAXS pattern of HDPE before uniaxial stretch. The scattering pattern is isotropic. It should be noted that the scattered intensity at such a low q region or submicron scale indicates the existence of larger scale density fluctuations than those of lamellar structures. In Fig. 2, the circularly averaged scattering profile $I(q)$ of HDPE before uniaxial stretch is plotted as a function of q.

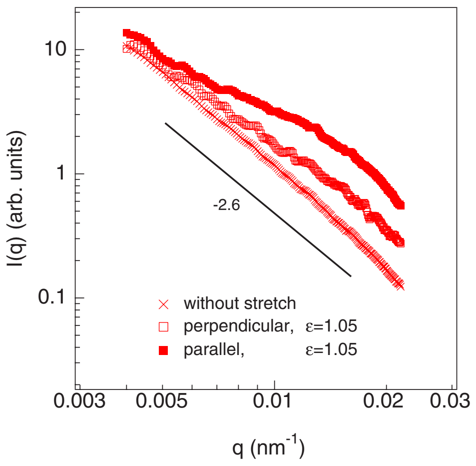

FIG. 2. (Color online) Scattering profiles parallel and perpendicular to the stretch direction are plotted as a function of q.

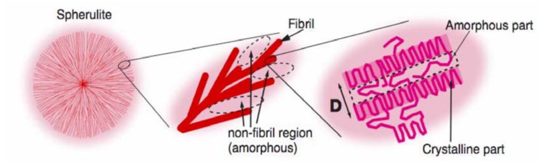

FIG. 3. (Color online) Schematic picture of the heterogeneity in spherulite. Spherulite consists of fibrils and the nonfibril region. Fibrils have lamellar structures of alternating crystalline and amorphous parts.

We found the power-law behavior expressed by

$$I(q) \sim q^{-2.6}. \tag{3}$$

The 2.6 value of the exponent is between 1 and 3, indicating that the long scale density fluctuations of spherulite obey mass-fractal. According to the studies on the growth of spherulite with electron micrograph by Vaughan and Basett [19], a sheaflike structure formed by an aggregate of layers appears at the center of the spherulite at the early stage of growth and then fibrils, composed of aggregates of layers, branch and splay to keep the increasing surface of the spherulite. Thus, this fractal property originates from the imperfection of volume filling by branching and splaying fibrils and the fibrils distribute in amorphous phase or less crystalline phase with mass-fractal feature as shown in Fig. 3. This fractal heterogeneity is similar to that in swollen gels although the swollen gel is less dense than crystalline polymers. It also should be noted that the 2.6 value of the exponent is similar to that obtained by percolation theory.

In Fig. 1(b), the 2D-USAXS pattern of HDPE after uniaxial stretch at $\varepsilon = 1.05$ is shown. The scattering pattern of the stretched HDPE has the shape of a butterfly pattern. The enhanced direction is along the stretch direction and the butterfly pattern observed in the stretched HDPE is thus an "abnormal" butterfly scattering pattern as observed in stretched heterogeneous gels and semidilute polymer solutions under shear flow. As mentioned previously, the sample does not contain any cavities or voids, thus the origin of the scattered intensity is the density fluctuations of HDPE. According to the cluster theory [3], the heterogeneous deformation causes the butterfly pattern. In crystalline polymers, the difference in deformation between fibrils and the nonfibril region corresponds to the heterogeneous deformation.

Figure 2 shows the scattering profiles parallel and perpendicular to the stretch direction plotted as a function of q. Here the scattering profile parallel to the stretch direction is obtained by sector average of the scattering pattern at $-5° < \varphi < 5°$ while the sector-averaged scattering pattern at $85° < \varphi < 95°$ corresponds to the scattering profile perpendicular to the stretch direction. It should be noted that the poor statistics of sector-averaged scattering functions originates from the speckle in the scattering pattern due to the small scattering volume. Although the intensity in both directions increases with the uniaxial stretch, the scattering profile parallel to the uniaxial stretch direction increases more strongly than the perpendicular one. The anisotropic increase agrees with the tendency observed in the case of

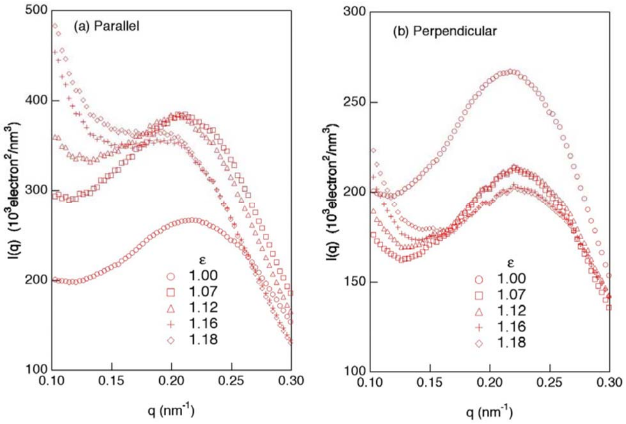

FIG. 4. (Color online) Changes in the SAXS profiles parallel (a) and perpendicular (b) to the stretch direction with ε.

swollen gels under uniaxial stretch. However, an increase in the direction perpendicular to the uniaxial direction is observed in the case of the stretched HDPE, while a decrease was observed for the swollen gels. This fact indicates that the density fluctuations are developed by stretching in the case of HDPE. According to Furukawa [20], if the spatial heterogeneity of stress field exists, the shear flow or stretch causes the density fluctuations due to stress-diffusion coupling even in one component liquid. In crystalline polymers, the viscoelastic property of fibrils is different from that in the nonfibril region. Thus, the development of density fluctuations by the spatial heterogeneity in stress field between fibrils and the nonfibril region changes the scattered intensity as well as heterogeneous deformation.

It is expected that the fibrils are less deformed than the nonfibril region since the fibrils are harder than non fibril region. Therefore, we investigated the changes in the lamellar structures of the fibrils after stretch, by using SAXS patterns in order to clarify the deformation of the fibrils with the uniaxial stretch. Figure 4 shows the changes in SAXS profiles parallel and perpendicular to the stretch direction with ε. Similar to USAXS profiles, scattering profiles parallel and perpendicular to the stretch direction are, respectively, obtained by sector average of the scattering pattern at $-5° < \varphi < 5°$ and $85° < \varphi < 95°$. The SAXS profiles exhibit the peak originating from the periodicity of the lamellar structures in the fibrils. We estimated peak positions q_m by fitting the SAXS profiles with the Gaussian function $I(q)=I_0 + A\exp\{-[(q-q_m)/w]^2\}$ with I_0, A, w, and q_m being floating parameters. The peak position $q_{m,\parallel}$ parallel to the stretch direction shifts to smaller q while the peak position $q_{m,\perp}$ perpendicular to the stretch direction shifts to larger q. The changes in peak position or domain spacing D calculated by

$$D = 2\pi/q_m \tag{3'}$$

reveal the change in the crystalline phases. Figure 5 shows $D_\parallel(\varepsilon)/D_\parallel(1)$ and $D_\perp(\varepsilon)/D_\perp(1)$ as a function of ε, where $D_\parallel(\varepsilon)$ and $D_\perp(\varepsilon)$ are, respectively, D parallel and perpendicular to the stretch direction. Contrary to our expectation, $D_\parallel(\varepsilon)$ increases with ε while $D_\perp(\varepsilon)$ decreases with ε. The solid lines in Fig. 4 were calculated with the assumption of affine deformation to the lamellar structures

$$D_\parallel(\varepsilon)/D_\parallel(1) = \varepsilon, \tag{4}$$

$$D_\perp(\varepsilon)/D_\perp(1) = \varepsilon^{-1/2}. \tag{5}$$

Although the changes in the spacing observed in the experimental results are slightly less than the calculated changes, $D_\parallel(\varepsilon)$ and $D_\perp(\varepsilon)$ have changed with the uniaxial stretch. This result indicates that the fibrils are well deformed by the uniaxial stretch. Surprisingly, the macroscopic scale does not follow affine deformation at all while the microscopic scale is nearly deformed with affine deformation. As already mentioned before, the origin of abnormal butterfly patterns is the heterogeneity of deformation. Here we found that the fibrils are well deformed. Thus the nonfibril region is less deformed than the crystalline region.

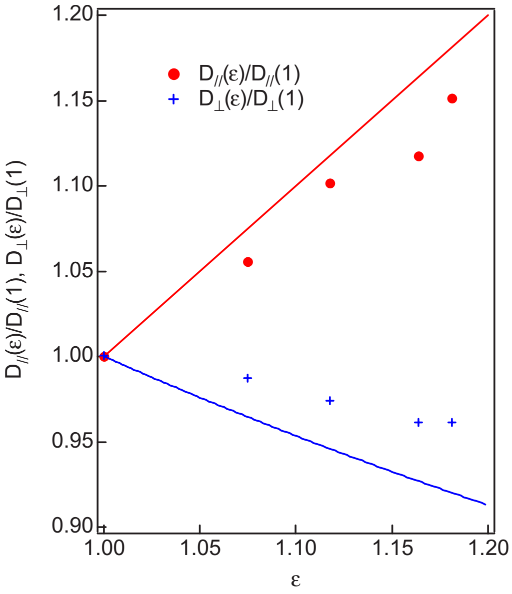

FIG. 5. (Color online) $D_\parallel(\varepsilon)/D_\parallel(1)$ and $D_\perp(\varepsilon)/D_\perp(1)$ as a function of ε. The upper and lower solid lines correspond to $D_\parallel(\varepsilon)/D_\parallel(1)$ and $D_\perp(\varepsilon)/D_\perp(1)$, respectively, calculated under the assumption of affine deformation.

IV. SUMMARY

In summary, we have investigated the density fluctuations in crystalline polymer HDPE under uniaxial stretch in the order of submicrons to microns with 2D-USAXS. After stretching, the isotropic scattering pattern was transformed into the butterfly pattern. The butterfly pattern is caused by heterogeneous deformation and stretch-induced density fluctuations. In heterogeneous deformation, the lamellar structures and fibrils are nearly deformed with affine deformation while the nonfibril region between the fibrils is not deformed as much. Stretch-induced density fluctuations are caused by the stress-diffusion coupling associating with the spatial heterogeneity in stress between fibrils and the nonfibril region.

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