Ultra small angle X-ray scattering studies on density heterogeneity of linear low density polyethylene

M Takenaka\(^1,2\), S Fujii\(^1\), S Nishitsuji\(^1\), N Yagi\(^3\), Y Suzuki\(^3\), and A Takeuchi\(^3\)

\(^1\)Department of Polymer chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, 615-8510, JAPAN
\(^2\)Structural Materials Science Laboratory, SPring-8 Center, RIKEN Harima Institute Research, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, JAPAN
\(^3\)SPring-8 JASRI, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, JAPAN

E-mail: takenaka@alloy.polym.kyoto-u.ac.jp

**Abstract.** We have investigated density heterogeneity of linear low density polyethylene (LLDPE) in the order of submicron scale with 2 dimensional ultra small angle X-ray scattering (2D USAXS). We found that power-law behaviour in small q-region of isotropic scattering patterns of LLDPE studied here, indicating that the density heterogeneity obeys mass fractal. Under stretching, isotropic 2D USAXS patterns of some LLDPE samples were transformed into butterfly patterns caused by heterogeneous deformation.

1. Introduction

Polyethylene (PE) is one of the common polymers used widely in our daily life. PE is a crystalline polymer and its physical properties strongly depends on the morphologies of crystalline or heterogeneity of density. PE forms a spherulite consisting of a hierarchical structure\(^1,2\). Among each level of structures, crystalline unit cell structure and lamellar structure have been well studied by using wide angle X-ray scattering (WAXS), and small angle X-ray scattering (SAXS) and obtained the characteristic parameters such as the degree of crystallinity, domain spacing of lamellar structures\(^3\). On the other hand, though the density heterogeneity in the order of sub micron scale in spherulite is thought to affect the mechanical properties of crystalline polymers, density heterogeneity in spherulite such as fibril structure has not been well investigated yet. This is because light scattering (LS) method, which is commonly used to observe the length scale from 100 nm to 1µm, can not be applied to investigate the density fluctuations of crystalline polymer having optical anisotropy in its crystal. However, the ultra small angle X-ray scattering (USAXS) camera with long path length and the synchrotron X-ray source has become available recently and it enables us to measure 2-dimensional (2D) USAXS pattern so that we can investigate anisotropic structure in submicron scale. In this study, we, thus, aim at the exploration of density heterogeneity of linear low density polyethylene (LLDPE) samples in the order of sub micron scale. Moreover, we would like to show how the stretch affect the density heterogeneity in the LLDPE samples. In our previous study\(^3\) on the density heterogeneity in the order of submicron scale for high density polyethylene, we found the isotropic patterns was transfored into butterfly pattern by stretching. The spatial heterogeneity of stress field or viscoelastic...
effects\(^{4}\) was found to induce the butterfly pattern, similar to the case of the butterfly pattern found in the chemical gel. We investigate whether the butterfly pattern appears in the case of LLDPE.

2. Experimental Section

2.1. Sample
We used three kinds of LLDPE: LLD-a (density 0.918 g/ml (25\(^{\circ}\)C), Melt Flow Index (MFI) 1.0 g/10 min (190\(^{\circ}\)C /2.16 kg), ALDRICH 428078), LLD-b (density 0.926 g/ml (25\(^{\circ}\)C), MFI 50.0 g/10 min (190\(^{\circ}\)C /2.16 kg), NEO-ZEX 25500J), LLD-c (density 0.931 g/ml (25\(^{\circ}\)C), MFI 26.0 g/10 min (190\(^{\circ}\)C /2.16 kg), NEO-ZEX 30200J). LLD-a includes hexene as a comonomer while butene is contained in LLD-b and LLD-c as a comonomer. The specimens are prepared by melt press method: First, the pellets of the samples were melted in a hot-press machine for an hour at 150\(^{\circ}\)C. Subsequently the samples were crystallized for 2 hours at 120\(^{\circ}\)C for LLD-a and 110\(^{\circ}\)C for LLD-b and LLD-c. Finally, the specimens were quickly cooled to room temperature with iced water. The sample thickness was set to be 2 mm. The samples were subjected to uniaxial extension at room temperature with the stretch rate being about 2.0\times10^{-3} \text{ sec}^{-1}. The elongation ratio \(\varepsilon\) is defined by

\[ \varepsilon = \frac{L}{L_0}, \]

where \(L\) and \(L_0\) are, respectively, the length of the sample after and before stretch.

2.2. USAXS experiment
We employed long path length (~150 m) and the synchrotron X-ray source at BL20XU, SPring-8 to investigate the density fluctuations in the order of the submicron scale. By using the setup at BL20XU, we can observed 2D scattering pattern at very small wave number \(q\)-region; \(0.005 < q < 0.02 \text{ nm}^{-1}\), where \(q\) is defined by

\[ q = \frac{4\pi}{\lambda} \sin(\theta/2) \]

with \(\lambda\) and \(\theta\) being wavelength of the incident beam and scattering angle, respectively. In this experiment, we used \(\lambda=0.05\) nm. To detect the scattered 2D intensity quantitatively, we employed the CCD camera with image intensifier\(^{5}\). The detail of the instruments was discussed elsewhere\(^{6}\). We
conducted the 2D USAXS measurement at room temperature.

3. Results and discussion

3.1. 2D USAXS patterns without stretching

Figures 1 and 2 show the 2D USAXS patterns for LLD-a and LLD-b without stretching. The 2D USAXS shows isotropic scattering patterns. Similar to the case of LLD-a and LLD-b, the isotropic scattering patterns can be observed in LLD-c. These results indicate that the density heterogeneity in the order of submicron scale exists in LLDPE. It should be noted that the scattered intensity at such low $q$-region or sub-micron scale indicates the existence of larger scale density fluctuations than those of lamellar structures. In Fig.3(a), we show the circularly-averaged scattering profile $I(q)$ of LLD-a and LLD-b without stretching plotted as a function of $q$. We found the power-law behavior expressed by

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

The 2.6 value of the exponent is between 1 and 3, indicating that the large scale density fluctuations of spherulite obey mass-fractal as shown in Figure 3. The mechanism to form the observed mass-fractal structure is not clear. However, as shown in the studies by Vaughan and Baselt with electron micrograph, a sheaf-like structure formed by an aggregate of layers appears at the center of the spherulite in early stage of the growth of spherulites and then fibrils, composed of aggregates of layers, branch and splay to keep the increasing surface of the spherulite. Thus, one of the possible origin of the mass-fractal density fluctuations is 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. It also should be noted that the 2.6 value of the exponent is similar to that obtained by percolation theory. In order to clarify the mechanism of the formation of the mass fractal structure, we need to investigate the time change in the scattered intensity during crystallization process with 2D USAXS.

3.2. 2D USAXS patterns after stretching

2D USAXS patterns for LLD-a and LLD-b after stretching are shown in Figures 4 and 5. In the case of LLD-a, the scattering patterns are elongated perpendicular to the stretch direction and becomes ellipsoidal patterns, indicating that the branch structure is elongated homogeneously. On the other hand, the scattering pattern of LLD-b exhibits butterfly patterns elongated parallel the stretch direction. This kind of butterfly pattern can be observed in the scattering patterns of shear-induced phase separation in semi-dilute polymer solutions.
In semi-dilute polymer solutions, the spatial heterogeneity of stress field induces associating with the concentration fluctuations since the dynamical properties of each component (polymer and solvent) are asymmetric. The heterogeneity of the stress field affects the free energy functional of the semi-dilute polymer solutions and causes the phase separation under shear field. Similarly, crystalline LLDPE has spatial heterogeneity of stress field associating with degree of crystallinity. Actually, the density fluctuations can be observed in 2D USAXS patterns of LLDPE without stretching. Under stretching, the heterogeneity of the stress field induces the density fluctuations and the butterfly patterns appear in the 2D USAXS.

There are two possible origins to explain the difference in behaviors in the scattered intensity under stretch between LLD-a and LLD-b and -c. One is the difference of molecular weight. In the case of LLD-a, MFI is much smaller than those of LLD-b and LLD-c, implying that the molecular weight of LLD-a is much larger than those of the others. Thus, the dynamical asymmetry between crystalline phase and amorphous phase of LLD-a is much smaller than those of the others and the small heterogeneity of the stress field did not induce butterfly pattern in LLD-a. Another possible origin is the difference of the comonomer. The comonomer of LLD-a is hexene while the comonomer of LLD-b and LLD-c is butene. The difference of comonomer may cause the difference of the mechanical properties of crystalline or amorphous phases. We need to investigate other LLDPE samples with 2DUSAXS further.

4. Conclusion
We have investigated density heterogeneity of linear low density polyethylene (LLDPE) in the order of submicron scale with 2 dimensional ultra small angle X-ray scattering (2D USAXS). We found that power-law behavior in small $q$-region of isotropic scattering patterns of LLDPE studied here, indicating that the density heterogeneity obeys mass fractal. Under stretching, isotropic 2D USAXS patterns of some LLDPE samples were transformed into butterfly patterns caused by heterogeneous deformation associating with the heterogeneity of the stress field induced by the dynamical asymmetry between crystalline phase and amorphous phase. In the case of high molecular weight LLDPE, the stretch induces the homogeneous or affine deformation and the butterfly patterns can not be observed. This is because the dynamical asymmetry is not enough to cause the density fluctuations.

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