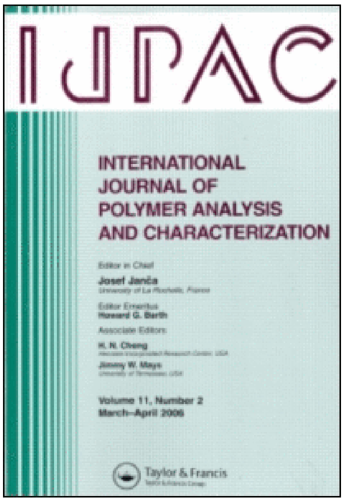

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Haifeng Shan[a]
[a] Department of Polymer Engineering, University of Akron, Akron, Ohio, USA

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Kinetics Study of Mesophase-Crystal Transformation in Highly Oriented Homogeneous Poly(ethylene-*co*-1-octene) Filament

Haifeng Shan
Department of Polymer Engineering, University of Akron, Akron, Ohio, USA

Abstract: The thermal stability of highly oriented homogeneous poly(ethylene-*co*-1-octene) (h-PEO) fiber during annealing process was carefully studied by time-resolved two-dimensional wide-angle X-ray diffraction (WAXD) pattern. The experimental results show that three phases exist in h-PEO fiber, orthorhombic crystal phase, pseudo-hexagonal mesophase, and amorphous phase, which are stable at room temperature. As soon as the fiber is heated, the mesophase transforms to orthorhombic crystal phase. This transformation kinetics was analyzed in terms of Avrami phase transformation theory. The Avrami index was found to be 1, indicating one-dimensional growth. This can be explained by the bundle-like crystal morphology existing in h-PEO.

Keywords: Avrami; Mesophase-crystal transformation; poly(ethylene-*co*-1-octene); Wide angle X-ray diffraction

INTRODUCTION

The new generation of polyethylene produced by single-site catalyst possesses a peculiar structure characterized by a narrow molecular weight distribution and homogeneous comonomer distribution at a uniform content along the molecules.[1,2] Also, it has lower density than conventional

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Correspondence: Haifeng Shan, Department of Polymer Engineering, University of Akron, Akron, OH 44325, USA. E-mail: haifeng_shan@yahoo.com

polyethylene, which offers a range of attractive properties such as lower module (higher flexibility), greater toughness, and lower heat seal initiation temperatures. These lower density polyethylenes show many interesting applications in the medical industry. For example, the extremely high catalyst activity may lead to materials with very low inorganic contamination, while the high comonomer content and random distribution provide superior optical clarity for particulate matter (PM) inspection.[3]

Many studies have been done on these copolymers, especially on crystal structure and morphology. Normally, polyethylene and its copolymers with higher density (above 0.9 g/cm^3) only have orthorhombic crystal structure. However, for these new copolymers with random distributed and higher content comonomer, some researchers observed an additional peak on wide-angle X-ray pattern.[4–6] These experimental findings indicate that there exists an intermediate phase, mesophase, between crystalline and amorphous fractions, which may be due to the one- or two-dimensional ordering of polymer chains. This phase usually refers to a wide spectrum of intermediate structures, ranging from stiff chains with no long-range registry to poorly formed crystals. There is not a clear boundary to delineate these regions.

Mesophase has also been found in other materials, such as polypropylene,[7] poly(ethylene terephthalate),[8] poly(ethylene naphthalate),[9] and poly(diethylsiloxane).[10] Usually, the mesophase is an unstable phase and will convert to more stable phase after annealing. Despite unambiguous evidence for its existence, there is still a lack of knowledge about its thermodynamic stability. In this work, we applied wide-angle X-ray diffraction technique to follow the continuing change of its content in homogeneous poly(ethylene-*co*-1-octene) upon annealing at isothermal conditions and studied its transformation kinetics. In order to observe mesophase clearly, the sample was melt spun at high draw-down ratio to reach high orientation degree. In this way, the mesophase and the crystal phase were concentrated at the equatorial position.

EXPERIMENTAL SECTION

The material used is ethylene-1-octene copolymer prepared by Dow's Insite® constrained geometry catalyst technology (CGCT). The density of the material is 0.870 g/cm^3. The comonomer content (weight percent) of copolymer was determined by Fourier transform-infrared (FT-IR) spectroscopy with the integral of the absorbance between 1381 and 1373 cm^{-1}, which is proportional to the number of -CH$_3$- groups. Accordingly, the 1-octene content of the investigated samples is 38 wt.% (13.3 mol%). The material was melt spun to get highly oriented fiber using high-speed spinning technique.

The time-resolved WAXD measurements were performed on Bruker AXS HI-STAR general area detector diffraction system (GADDS).

A temperature controller was added to the X-ray apparatus for thermal WAXD measurements. Nitrogen gas was purged to prevent oxidation. Monochromatic CuKα ($\lambda = 1.54$ Å) radiation was used. The sample-to-detector distance was 12 cm, and the sample stage was set to capture one unique quadrant of the WAXD pattern. The generator settings were 40 kV and 40 mA. A bundle of fiber about 1 mm thick was kept at 35°C for 500 min. One complete exposure requires 60 s. The d-spacings were calibrated with silicon power (325 mesh size).

RESULTS AND DISCUSSION

Figure 1 shows a series of 2-D WAXD patterns of the homogeneous poly(ethylene-*co*-octene) (h-PEO) fiber taken at different times while being annealed at 35°C. The concentration of peak at the equatorial position indicates the high orientation of the sample. The azimuthal width of the (110) and (200) peaks remains constant at different times, which means there is no relaxation happening during annealing. Two peaks, which are located at 4.2 and 3.8 Å, were identified as (110), (200) peaks from orthorhombic crystal structure. There is an additional peak located at amorphous halo position at 4.5 Å. This peak may be from either amorphous phase itself or mesophase. If we assume it is from amorphous phase, then we must answer the question: can amorphous phase be oriented so highly? Oda et al.[11] investigated the orientation of atactic polystyrene (a-PS) during melt spinning. The maximum orientation factor it can reach was only about 0.04. However, from our previous study,[12] the orientation factor of this phase was about 0.6. Also, h-PEO has much lower glass transition temperature than a-PS, which means h-PEO has shorter relaxation time. It is thus more difficult for it to maintain such high orientation degree during melt spinning. We thus ascribed this new peak to mesophase. Similar mesophase has been observed under other conditions. Pennings and Zwijnenburg[13] observed similar hexagonal mesophase in polyethylene fibers, when the fiber was heated above the normal melting temperature with both ends being fixed to prevent retraction. The reduced configuration entropy of constrained melt is clearly responsible for the hexagonal phase being more stable than the melt in this case. From comparing the patterns in Figure 1, we can also see that during annealing, the amount of mesophase became less, while the amount of crystal phase became enriched. This tells us there is a mesophase-crystal phase transformation happening during annealing.

In order to calculate the amount of mesophase, we integrated the intensity of the 2-D WAXD pattern and plotted it against 2θ in Figure 2. GRAM32 software was used to decompose the pattern into orthorhombic crystal phase ((110) and (200) crystal peaks), mesophase,

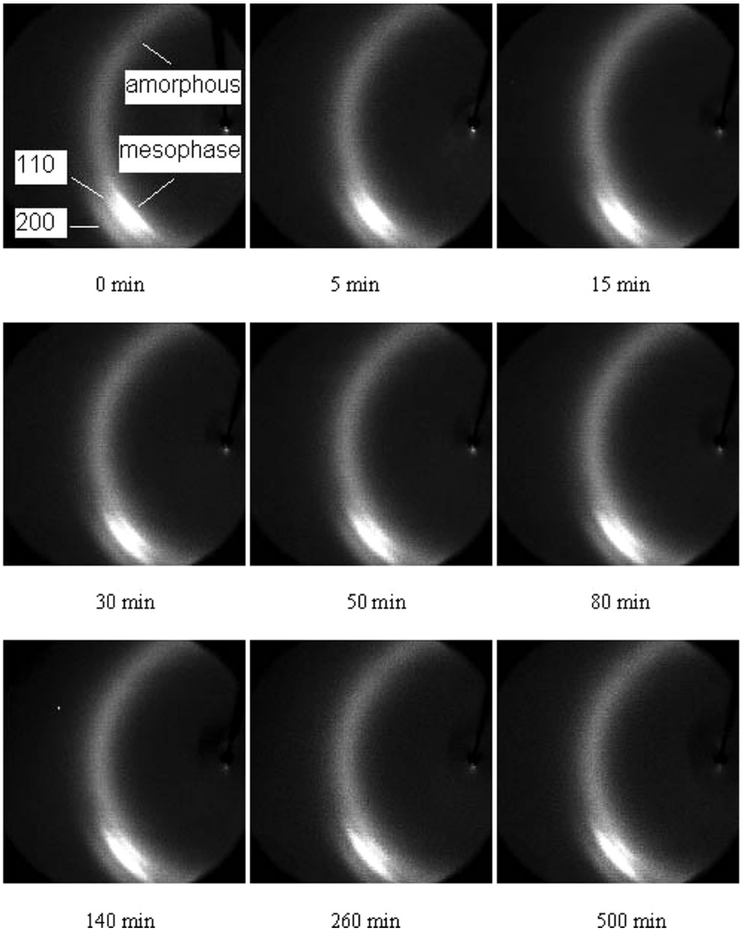

Figure 1. WAXD pattern for samples annealed at 35°C for different times.

and amorphous phase. A symmetrical function consisting of Gaussian and Lorentzian profiles for each peak was assumed. The ratio of I_{110}/I_{200} was fixed at 3.1, which is the theoretical value for orthorhombic polyethylene.[14] The amount of amorphous phase (I_a) was assumed to be unchanged. The relative content change of mesophase (ϕ_m) and crystal phase (ϕ_c) was thus calculated, via Equations (1) and (2), and plotted against time in Figure 3:

$$\phi_m = \frac{I_m}{I_{110} + I_{200} + I_m + I_a} \tag{1}$$

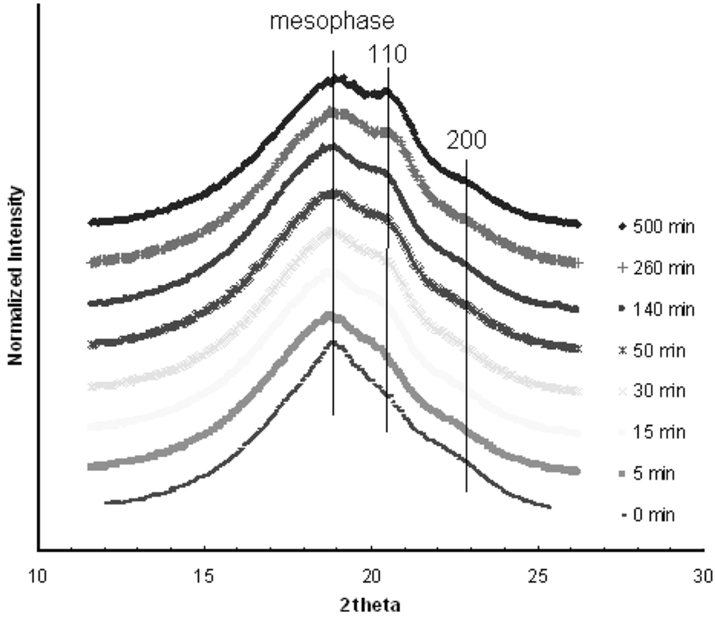

Figure 2. Intensity-2θ curves after integration (one-quarter pattern).

$$\phi_c = \frac{I_{110} + I_{200}}{I_{110} + I_{200} + I_m + I_a} \tag{2}$$

It can be seen that the relative content of mesophase shows an exponential decrease with time, while the relative content of crystal phase shows an exponential increase. The obtained extent of crystal phase was further analyzed in terms of the Avrami equation. On the basis of the Evans theory, Avrami proposed the phase transformation theory, which has been successfully applied in the crystallization process. According to this equation, when a polymer crystallizes from a melt, the degree of crystallinity, X_t, is related to time, t, in the form of

$$1 - X_t = \exp(-Kt^n) \tag{3}$$

where X_t is the relative amount of crystallinity at time t, K is the crystallization rate constant containing nucleation and crystal growth rate constants, and n is the Avrami exponent related to the crystallization mechanism. We shall use this approach to describe the mesophase transition kinetics during annealing of h-PEO. The log-log fit of the content of mesophase using Equation (1) yields a slope, i.e., the power n, of 0.8 (rounded off to 1; Figure 4).

It is interesting to note that a value of $n = 1$ is identical to that found in earlier studies of the crystallization of natural rubber that had been

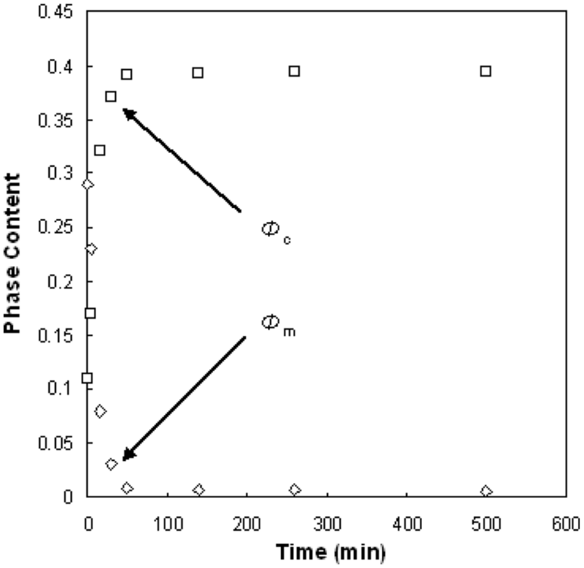

Figure 3. Phase content as a function of time during annealing at 35°C.

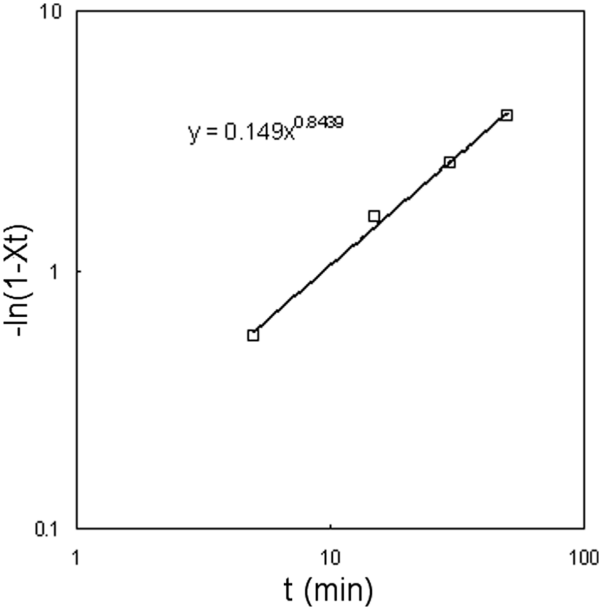

Figure 4. Avrami plot of $X_t = (\phi_{ct} - \phi_{c0})/(\phi_{c\infty} - \phi_{c0})$ against time t during annealing at 35°C.

rapidly stretched to high draw ratios at low temperature.[15] The straightforward interpretation in terms of the Avrami equation would be that the crystallization process is associated with the growth of entities in one dimension from preexisting nuclei. This would conform to the model originally proposed by Flory[16] for fibrous crystal growth in the direction of strain. The kinetics is characteristic of oriented polymers when a substantial fraction of the chain segments are fully extended. It is distinct from the case of intermediate orientation where a small fraction of extended chains can lead to row nucleation and to shish-kebab crystal morphology.[17] Transmission electron micrograph (TEM)[18] and atomic force micrograph (AFM)[19] observations revealed bundle-like crystal morphology in h-PEO in previous studies. Our WAXD results confirm the kinetics of bundle formation.

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