

Shear effects on crystallization behavior of poly(ethylene-co-octene) copolymers

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Abstract Crystallization behavior of sheared polymer melts of a series of poly(ethylene-co-octene)s with different octene content was investigated by different scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and synchrotron small-angle X-ray scattering (SR-SAXS) techniques. The DSC results indicated that the hexyl branches content had dramatic effects on the thermal properties and crystallinity of polyethylene. It was also found that shear had no obvious effects on the size of either crystallite or lamellae. However, both crystallite and lamellae were oriented by shearing, especially for the lamellae. All obtained results indicate that the initial states of the polymer melt play an important role in affecting the crystallization behaviors. The difference of the shear-induced crystalline structure evolution and the orientation between crystallite and lamellae support the preordered mesomorphic phase of flexible polymer crystallization process proposed by Strobl.

Keywords Poly(ethylene-co-octene) copolymer · Shear induced crystallization · Ethylene sequence length distribution · Mesophase

Introduction

The geometrical nature and mechanism of polymer crystallization of flexible chain molecules was in a state of intense discussion for a long time [1–5]. Crystallization in polymer systems, which transfers the entangled melt into a semi-crystalline state, is a process of primary importance and has been studied for a long time. Different from low molar mass compounds, it is difficult for polymer systems to form perfect crystals but they usually end up in a metastable state which is crystalline in parts under ordinary conditions. A semi-crystalline polymer crystallized from the melt is usually composed of lamellar crystallites which are separated by amorphous layers. Structure parameters, like the volume fraction of the crystallites or their thickness, are kinetically controlled and change with the crystallization conditions. In the range of crystallization temperature, usually crystallites are thicker when crystallization temperature is increased which is accompanied by a decrease in the rate of crystallization. Studies of polymer crystallization ask for an understanding of these dependencies based on the knowledge of the molecular processes controlling the transformation [2].

Investigations of the kinetics of polymer crystallization are usually carried out with the aid of polarized optical microscopy (POM), differential scanning calorimetry (DSC), SAXS, WAXS, dilatometry, time dependent vibrational spectroscopy or light scattering experiments. Although based on different properties and probing different physical values to derive information about a sample's crystallinity, all these methods end up having a similar sensitivity: reliable data can only be

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obtained for crystallinity already in the range of some percent of the final value. Reaching an end size on the order of several microns, the earliest growing spherulites which can be detected by these measurements already have sizes of several hundred nanometers. However, this is far away from the initial stages of spherulite nucleation and growth.

These early stages have recently gained particular importance in the discussion of the basic mechanisms of polymer crystallization [3–5]. There are several experimental observations that lead to the assumption of a crystal nucleation and growth which includes an intermediate phase, although a commonly accepted view has not yet evolved. Some authors propose a preceding coverage of the whole volume by a mesomorphic phase which develops by a mechanism resembling a spinodal process [3] while others point at indications for a nucleation into a mesomorphic phase followed by transformation into a crystal [4, 5].

A range of ethylene copolymers have been produced by metallocene-catalyzed copolymerization of ethylene and various linear 1-alkenes before [6, 7]. It has been well established that the properties depend more on the content of comonomer than chemical nature of the co-units, such as 1-butene, 1-hexene, and 1-octene [8–12]. With increasing comonomer content, the morphology of the crystals changes from lamellar structure with limited lateral dimensions to granular crystals, and then to an assembly of defect-rich, fringed micellar crystals [13, 14]. In the ethylene copolymer, the macroscopic properties, such as the degree of crystallinity, crystallization behavior and melting behavior, to a large extent depend on the specific arrangement of the short branches along the backbone and the branches content [11].

The short branches in the copolymer can give rise to a distribution of crystallizable ethylene sequence in the chains, defined as ethylene sequence length distribution (ESLD), which has a great influence on the physical parameters according to the thermodynamic model of Flory [15]. Based on that, the sequences with comparable length are favored to aggregate to form crystals during the process of crystallization and other incomparable sequences will be retarded from crystallization. Furthermore, bulky aliphatic branches with six carbon atoms or more are expelled from the crystal lattice and, reversely, the shorter chain branches will hinder the crystallization of ethylene units [16].

When crystallization occurs in polymer melt, it is idealized that all sequences with comparable length merge into extended-sequence crystallites of a related thickness with infinite lateral dimension [17]. However, the complete selection and segregation of ethylene sequences is never reached for a large number of restrictions. For instance, in reality, once the longest sequences have crystallized, diffusion of shorter sequences to appropriate crystal fronts is increasingly frustrated [9]. Another illustration is that the mobility of ethylene sequences of the same molecules in the amorphous phase will be gradually

decreased when other sequences have incorporated into crystals [18]. In a word, the structure and therefore the properties of the poly(ethylene-co-octene) copolymer, which are adjustable by the variation of hexyl branches concentration, is complicated and still worthy to study for both theoretical reasons and the commercial interest for the effect of processing. Besides these micro-structural parameters, sample conditions such as external field (shear, pressure) and thermal history during the processing are crucial factors which would influence the crystallization development and the ultimate product properties. Many studies by scattering techniques, such as SAXS and WAXD, have been utilized for the copolymer to investigate the crystallization morphology, structure and mechanical properties [18–21] at different temperatures and pressures. However, it is still not well known how the crystallographic structure of the ethylene copolymers with different alkene content is influenced under shear. Relatively speaking, the polymer processing by injection molding, a short shear pulse is deemed to be a better approach to investigate the initial crystallization process. In this work, we report studies of the crystallization multi-scale structures based on WAXD and SR-SAXS measurements performed on a series of ethylene-1-octene copolymers crystallized with a step-shear process. The present objective was to look into the side branch content effects on the shear-induced melt crystallization behavior and resulting structures and provide a new clue to understanding the structure evolutions during crystallization in ethylene-octene copolymers.

Experimental section

Ethylene-octene copolymers of the metallocene catalyst type with different octene contents including 2%, 7%, 12%, 14% and 25% weight percent of octene co-units (0.5, 1.8, 3.3, 3.9 and 7.7 mol%), produced by Dow Chemicals Europe, are named as PEcO2, PEcO7, PEcO12, PEcO14 and PEcO25, respectively. A Linkam CSS450 shear hot stage was used to control the temperature and shear rate. The sample was first melted and kept for a certain time to eliminate any residual thermal effects, then cooled to a crystallization temperature with a rate of -30 K/min. The thickness of the samples was adjusted to $1,000$ μm . The crystallization temperatures were set to 120, 105, 97, 92 and 40 $^{\circ}\text{C}$ for PEcO2, PEcO7, PEcO12, PEcO14 and PEcO25, respectively. During this process, a 5 s step-shear with different shear rates was applied to the samples as soon as the isothermal crystallization temperature was reached. Samples of PEcO7 and PEcO14 were chosen for in-situ synchrotron SAXS observations. The samples were fixed two steel slices covered with Kapton tape for X-ray investigations. The samples were heated into the isotropic melt phase first, and then cooled to the preset crystallization temperature. When crystallization temperature was reached,

a 5 s shear with shear rate 2 s^{-1} was applied to compare with the crystallization process without shearing. The crystallization processes were recorded by time-resolved synchrotron SAXS.

Thermal experiments for the samples after isothermal crystallization were carried out with a Perkin-Elmer DSC-7 apparatus in a dry nitrogen atmosphere. The temperature and heat flow were calibrated with an indium standard. The sample masses were typically approx. 4–6 mg. The heating and cooling programs were controlled with a rate of 10 K/min.

WAXD results for the samples after isothermal crystallization (no-sheared samples as shown in Fig. 2 and sheared samples in Fig. 3, and the shear rate was 5 s^{-1} , 10 s^{-1} and 20 s^{-1}) were obtained with a Rigaku D/max 2,500 V PC X-ray diffractometer (Japan) with a $\text{CuK}\alpha$ source working at 40 kV and 200 mA. Scattering angle (2θ) was chosen from 10° to 40° , and the step was 0.02° . For 2D WAXD, an imaging plate with a dimension of $127 \times 127 \text{ mm}$, provided by Fuji Photo Films Co. Ltd., was used. The exposure time was 30 min.

SAXS measurements were carried out at synchrotron beam line BL15A of the photon factory (PF) of the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The X-ray wavelength at BL15A is 1.54 \AA . SAXS patterns were recorded for 2 s exposure with the detector located at a distance of 2,100 mm from the sample position. In-situ experiments were performed at beamline 1W2A of Beijing Synchrotron Radiation Facility (BSRF), Beijing, China. The wavelength was 1.55 \AA and the distance from detector to the sample position was 3,050 mm. All data were corrected for background scattering before analysis and treated with the software Fit 2D [22].

Results and discussion

For the physical properties of ethylene-1-octene copolymers, such as crystallinity and mechanical behaviors, depend on the molecular structure and molar mass distribution, especially on the ethylene sequence length distribution (ESLD). As seen the DSC results in Fig. 1 (for the samples after isothermal crystallization without shearing), the content of octene have a dramatic influence on the thermal behavior as seen in the melting and crystallization peaks. The reduced DSC peaks area denotes lower crystallinity with higher content of octene comonomers. During cooling at ambient pressure, the distribution of crystallizable ethylene sequences, based on the ESLD in the copolymer, leads to a distribution of crystallization temperature and thus a crystallite size distribution in the copolymer. The crystalline sequences from the ESLD decrease with the increase of the branch content. Meantime, crystallization is more difficult which caused the decrease of crystallization temperature and a broader crystallization range in DSC cooling curves (see

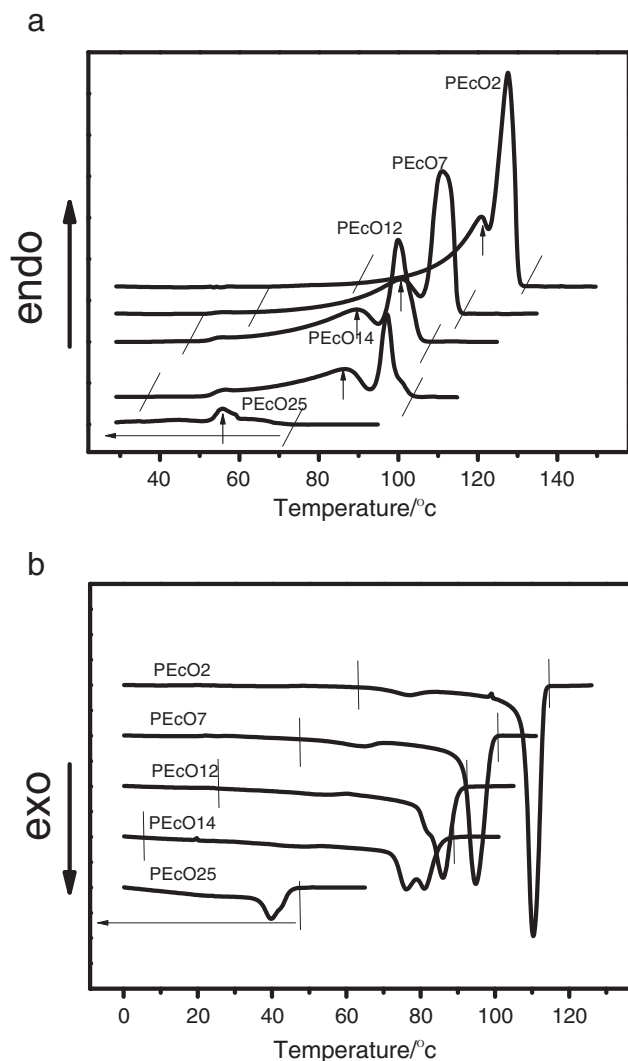


Fig. 1 DSC curves of PEcOx after isothermal crystallization (Slashes in the figure means the range of melting temperature and crystallization temperature). **a** heating curves at a rate of 10 K/min; **b** keeping above melting point for 5 min, afterwards, cooling curves at rate of -10 K/min

Fig. 1b). For thermodynamic reasons, the crystallites with different size will melt at different temperatures during heating, resulting in a low melting temperature and a broader distribution in the DSC curves (see Fig. 1a).

One can see that multiple melting peaks also appeared for both melting and crystallization curves. It is common for semi-crystalline polymers to possess multiple melting peaks. Generally, they have three explanations: firstly, different melting temperature for different lamellar thickness; secondly, the transform of relative small and defective crystal to larger and more perfect one after melting and recrystallization; thirdly, the melting process of different crystal forms. It has been reported that two different types of crystals for ethylene-octene copolymer are formed by different crystallization mechanisms, lamellar and fringed-micellar crystals which can be related to the relatively sharp

high temperature part of the melting peak (largely irreversible melting) and the broad lower-temperature endothermic region (reversible melting), respectively [8, 23, 24]. For the investigated copolymers, we considered that the multiple peaks should be ascribed to different distributions of crystals with different thermodynamic stability. We thought that the smaller peak (see Fig. 1a, arrows) probably resulted from annealing at ambient temperature because it decays during the second heating scan. From Fig. 1b one can see that the ethylene-1-octene copolymers displayed a sharp high temperature peak followed by a broader secondary one (except for sample PEcO12 and especially obvious for sample PEcO14, the peak at high temperature splitted into two peaks). With the increasing branches the high temperature exothermic peak fades away and low-temperature exothermic peak broadens, grows, and finally extends down to the glass transition at the highest comonomer contents [18]. The high-temperature exothermic peak has been related to classical chain-folded lamellae from unconstrained, non-pinned crystallite sequences and the low-temperature one to the formation of very small crystallites, including block like entities and fringed micelles, from a constrained melt in the confined amorphous nanophases between the already existing crystals. As for sample PEcO12 and PEcO14, there shows a shoulder at 82 °C beside the peak at 86 °C and at 76 °C beside 81 °C, respectively. This phenomenon was special and the reason is unknot well known to us at present. We considered that the phenomenon might be ascribed to two competitive results of decreasing comonomer branches content in the crystallization system, the first result was ascribed to the decreased branches which tangled with ethylene crystallization bone chain. To some extent the crystalline sequences might be folded more easily for the less twists of crystallizable long chains which conduced the crystallization process more easier to carry out; The other was that decreasing branches caused longer ethylene sequences in main chain which could entangled each other. Based on that, it enhances the difficulty for ethylene bone chains to crystallize [11, 25]. We deemed that the splitted

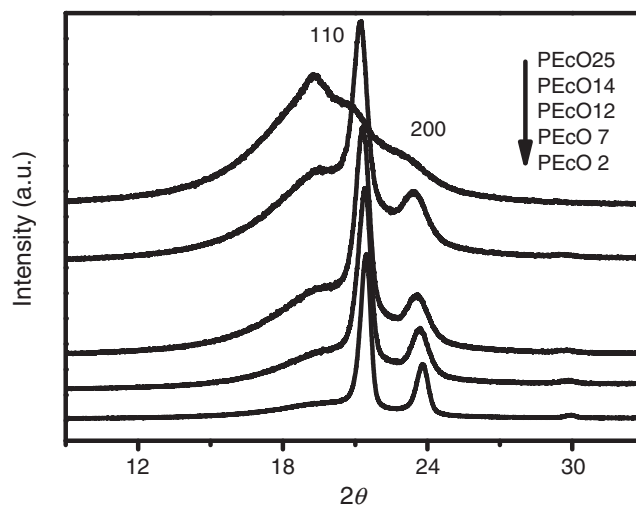


Fig. 2 WAXD of PEcOx after isothermal crystallization

two peaks came from the unstable crystallization system for the competitive crystallization processes. In a word, the most important factor influencing the position and size of the DSC crystallization and melting curves is ascribed to the comonomer content which determines the ESLD.

The peak positions in DSC endotherm curves are related to the hexyl branches content and their degree of incorporation in the ethylene backbone chains, which influence the final crystallites size, perfection and stability. WAXD is a primary method to characterize the physical features such as crystalline structure, crystallite size and crystallinity. As shown in Fig. 2 (samples of PEcOx after isothermal crystallization without shear), the amorphous peak area increased with increasing short-chain branches denoting the decreasing crystallinity. The influence of short-chain branches on the crystalline ability of ethylene backbone units is more and more obvious with the increasing branches and the decreasing crystallinity can be attributed to the increase of the concentration of ethylene sequences which are too short to crystallize. The diffraction peaks in the WAXD profile at 21.4° and 23.7° which are assigned to the 110 and 200 reflections of the orthorhombic

Table 1 Structure parameters of PEcOx

	DSC results			WAXD results					
	Melting point/°C	Crystallization point/°C	Crystallization temperature/°C	Crystallinity/%	110 reflection		200 reflection		
					2θ	size/nm	2θ	size/nm	
PEcO2	129	110	120	75	21.8	18.6	24.2	17.5	
PEcO7	112	95	105	60	21.8	13.9	24.1	10.6	
PEcO12	101	86	97	46	21.7	12.4	24.0	9.6	
PEcO14	95	81/76	92	39	21.6	11.8	23.9	8.3	
PEcO25	42	40	40	17	23.5	5.5	21.5	4.3	

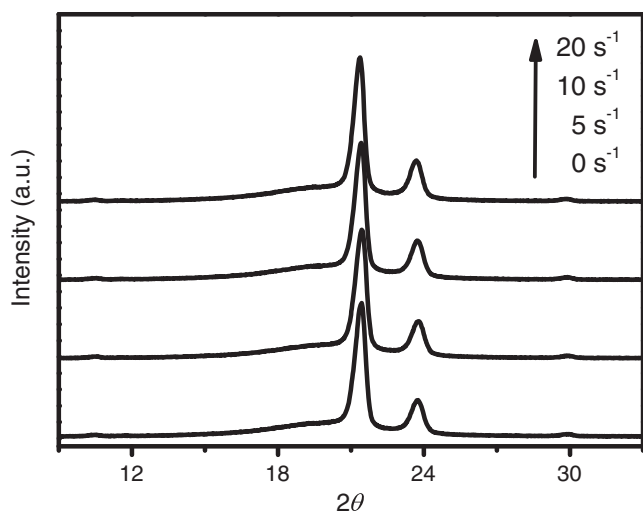


Fig. 3 WAXD curves of PEcO2 after isothermal crystallization at 120 °C with different shear rate

phase become less pronounced with the increasing branches. There also shows an additional sharpness of the amorphous peak at about 19.7° which has been reported before [26–28] and it is more obvious with increasing branches in the obtained results. However, its nature has not been well understood. Some researchers assigned the additional reflection to the hexagonal mesomorphic phase which is not stable at room temperature and could probably be stabilized by the form of hexyl branches [26, 27] and some others have assigned it to a monoclinic crystallization phase reflection [28]. As an overview, it is caused by bulky aliphatic branches which cannot be incorporated in an orthorhombic PE crystal and consequently form some other kinds of “crystal” with an order nature intermediate between crystalline and amorphous [19, 29].

One can see that the positions of the two reflections in Fig. 2 move to the lower 2θ angle with the increase of branching content. It has been reported that by heating or under released pressure the orthorhombic crystalline reflections of ethylene-1-octene copolymer would shift to lower 2θ angle because of the looser packing of the chain sequences pointing to an increase in unit cell parameters [10]. In present results, the relatively loose packing of the chains in the unit cell within the crystal can be attributed to the incorporation of the hexyl branches into the ethylene backbone,

and the effect is aggravated with more and more branches. The variation of corresponding melting temperature, crystallization temperature (from DSC), crystallinity and crystallite size of 110 and 200 reflections (from WAXD) for the series of samples without shear are listed in Table 1. The methods for determining the degree of crystallinity and the crystallite size of the 110 and 200 reflections were peak-fit procedure; the detailed procedure was the same as that used in our previous work [30]. With an increase of the comonomer content, the crystallite size decreased which was consistent with the results of lower melting temperature. Both WAXD and DSC indicate crystalline phase in the copolymers, except for the sample PEcO25 which is almost an elastomer.

To study the shear effects on the crystalline structure, WAXD curves and 2D WAXD patterns were obtained as shown in Figs. 3 and 4. From the WAXD curves of PEcO2 after isothermal crystallization with different shear rates, one can see that the shear did not affect the crystalline form and had no influence on the crystallite size. In Fig. 4, the two diffraction rings from inside to outside correspond to the 110 and 200 reflections. With increasing shear rate the crystallite reflections gradually display orientation, and especially it is more distinct for 110 reflections. The detailed azimuthal intensity distributions of the reflections are shown in Fig. 5. The crystallite orientation was strengthened with increasing shear rate. Similar to PEcO2, the other samples showed the same trend of crystalline orientation. Once shear was imposed, some polymer chains in the melt will undergo a coil-stretch transition and when the external field ceased, the chains could relax back to the initial state or grow and align inducing the subsequent crystallization. The competition between the relaxation of polymer chains and crystallization determines the final crystalline structure. Higher shear rate induces a higher degree of chain orientation and the final higher oriented structure after crystallization. At the same time we also noticed that under the same shear field the degree of crystallite orientation became more and more indistinct with the increase of branches content. We know that the mobility of ethylene polymer chains decreases with increasing branches, and that the decreasing backbone mobility hinders the influence of shear on the chains orientation. In

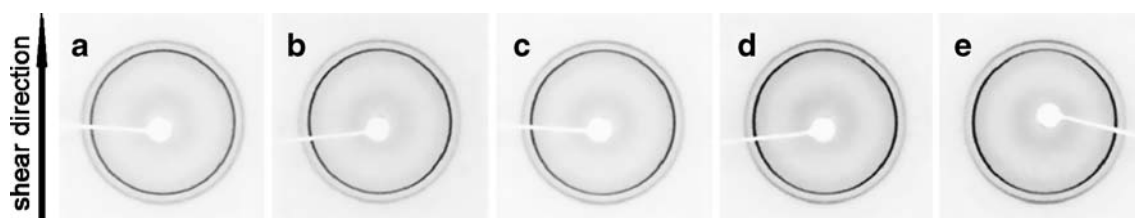
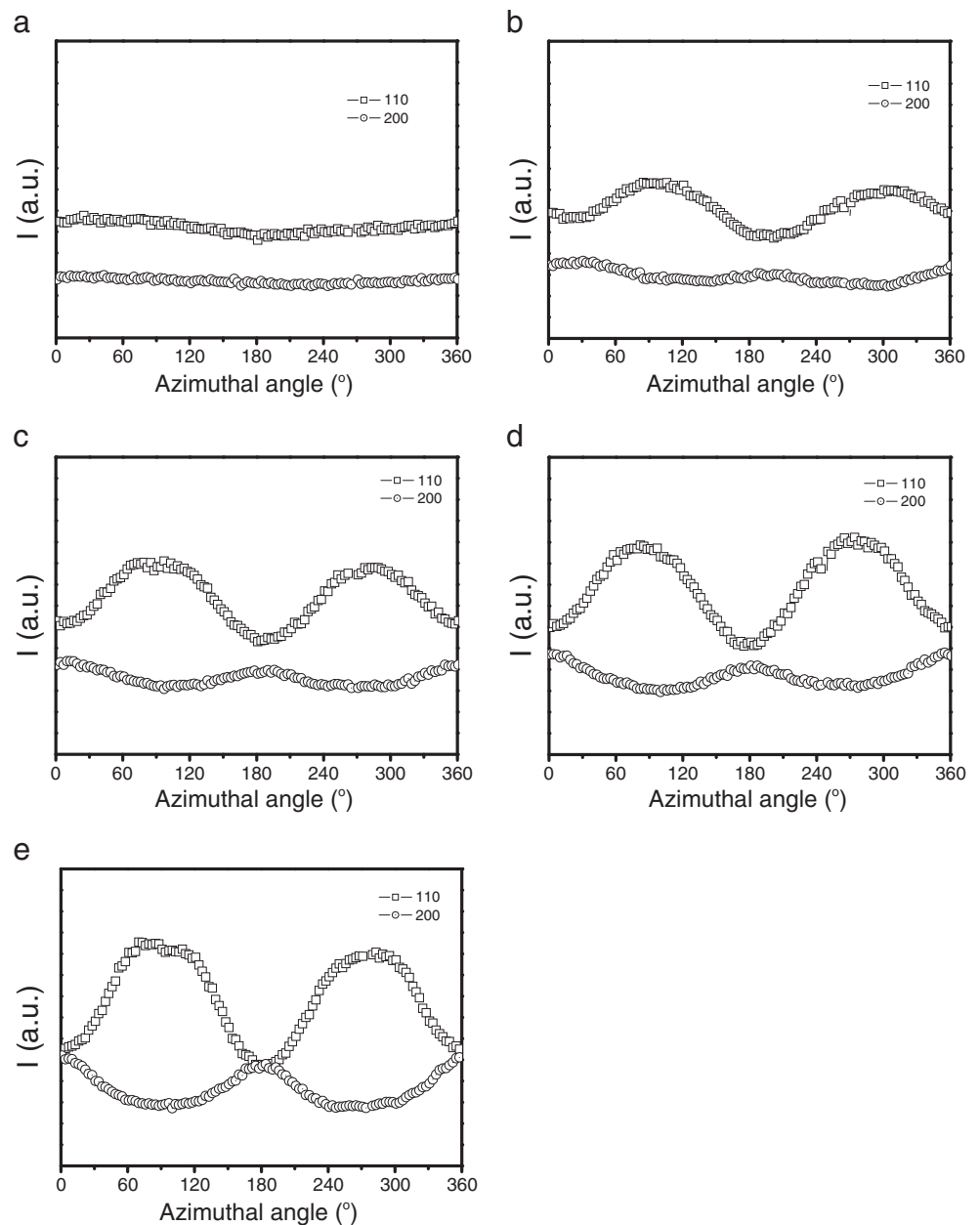


Fig. 4 WAXD patterns of PEcO2 after isothermal crystallization at 120 °C with shear rate, **a** 0 s⁻¹; **b** 2 s⁻¹; **c** 5 s⁻¹; **d** 10 s⁻¹; **e** 20 s⁻¹

Fig. 5 Azimuthal angle intensity of 110 and 200 reflections for PEcO2 after isothermal crystallization at 120 °C with shear rate, **a** 0 s⁻¹; **b** 2 s⁻¹; **c** 5 s⁻¹; **d** 10 s⁻¹; **e** 20 s⁻¹



the mean time, the structure is distorted by the crystal defects caused by ethylene sequence chains with broader distribution

and the incorporation of increasing numbers of branches [31]. Polymer chains composing the crystalline structure seem to be

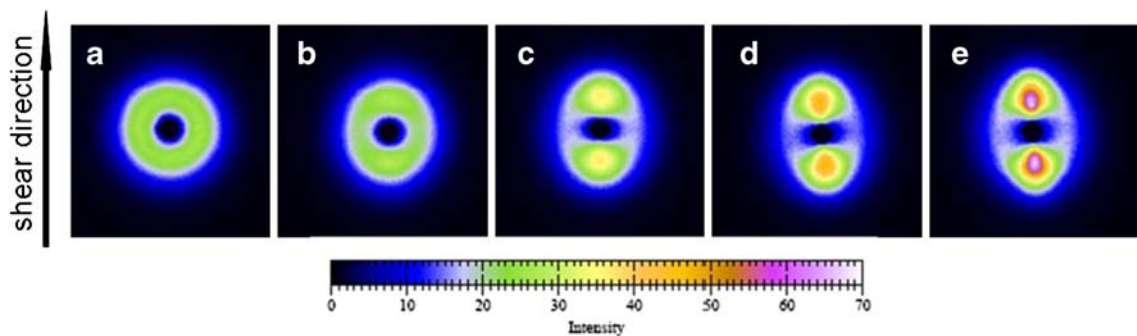


Fig. 6 SAXS patterns of PEcO7 after isothermal crystallization at 105 °C with different shear rate, **a** 0 s⁻¹; **b** 2 s⁻¹; **c** 5 s⁻¹; **d** 10 s⁻¹; **e** 20 s⁻¹

“frozen up” with high content of branches which is responsible for the weak orientation degree of crystallite structure.

Detailed information about lamellar structure parameters, such as long period and lamellar thickness, can be obtained by

SAXS technique. All SAXS analysis depends on assumptions that there exists a two-phase morphology including lamellae. For a number of ethylene copolymers, Mathot et al. have observed the existence of lamellae via staining of the

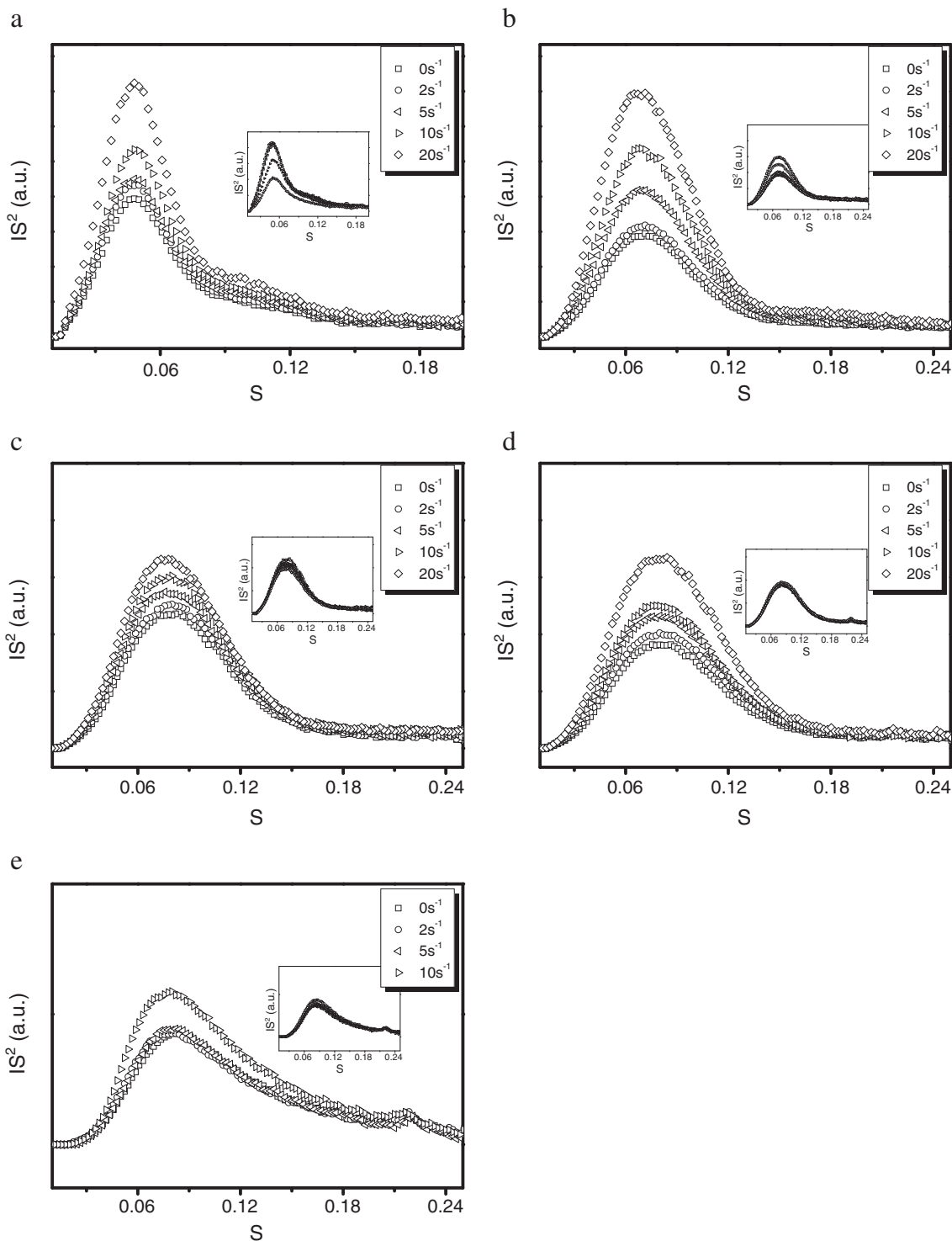


Fig. 7 IS^2 versus s of PEcOx after isothermal crystallization at different shear rates along the meridian (Insertion is the relationship along the equator): **a** PEcO2 with crystallization temperature 120 °C; **b**

PEcO7 with crystallization temperature 105 °C; **c** PEcO12 with crystallization temperature 97 °C; **d** PEcO14 with crystallization temperature 92 °C; **e** PEcO25 with crystallization temperature 40 °C

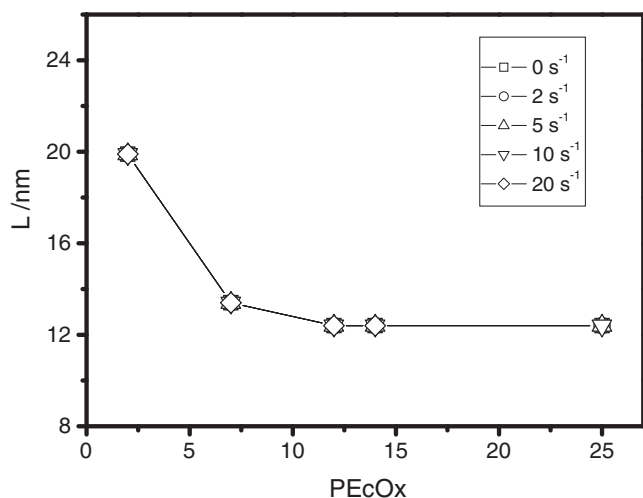


Fig. 8 Long period (L) obtained from SAXS data of PEcOx after isothermal crystallization with different shear rate

amorphous phase as observed by TEM [32] and stated that there was no reason to assume a third phase because the two-phase model was adequate. In such cases, the average distance between the lamellae brings the periodic fluctuation in electron densities which can be measured by SAXS. Figure 6 shows SAXS patterns of sample PEcO7 after isothermal crystallization with different shear rates. Shear direction is denoted by the arrow. Shear direction and the direction perpendicular to shear direction are termed meridian and equator, respectively. When the sample crystallized without shear, the scattering ring was isotropic, whereas the scattering rings for sheared samples were anisotropic and the orientation degree increased with strengthened shear. From the SAXS patterns one can see that most oriented lamellae align parallel to the equator. Figure 7 shows the relations between corrected intensity $I s^2$ with s from the SAXS patterns. According to the Bragg's law, $L = 1/s_{max}$, where L is the period of adjacent layers

(lamellae) and the s_{max} ($s = 2\sin\theta/\lambda = q/2\pi$, 2θ denotes the scattering angle, λ is the wavelength of X-ray and the modulus of the momentum transfer vector q) represents the peak position in the Lorentz corrected scattering intensity plot. For the copolymer with the same branches content, the long period was not influenced by shear rate (Fig. 8).

With the increasing of shear rate, the SAXS intensity along the meridian became stronger whereas it became weaker along the equator. With the SAXS intensity arising from the difference in the density of scatter and the surrounding medium, the stronger scattering intensity indicates an enhancement of the amount or greater perfection of the lamellae oriented perpendicular to the meridian. The SAXS peaks incline to be broader with enhanced content of hexyl branches which can be attributed to a broadened lamellae distribution. Furthermore, the s_{max} shifts to higher value with the increasing amount of branches denoting the decrease of long period. It can be due to the result of the reducing ethylene sequences length capable of crystallization.

To obtain detailed information about the structure parameters, such as long period L and average lamellar thickness L_c , the one-dimensional electron intensity correlation function $K(Z)$, which can be derived from Fourier transform of the scattering curve, was adopted to learn the influence of shear on the structures [33].

$$K(Z) = \frac{1}{2\pi} \int_0^{\infty} I(s)s^2 \cos(sZ) ds \quad (1)$$

We discuss the lamellar structure parameters along the meridian and the equator which are related to the statistical value of the lamellar parameters. Figure 9 shows the detailed structural parameters L_c of the samples after isothermal crystallization with different shear rates in both directions, calculated according to Eq. (1). Lamellar thickness L_c decreases with the increasing of octene content just the same

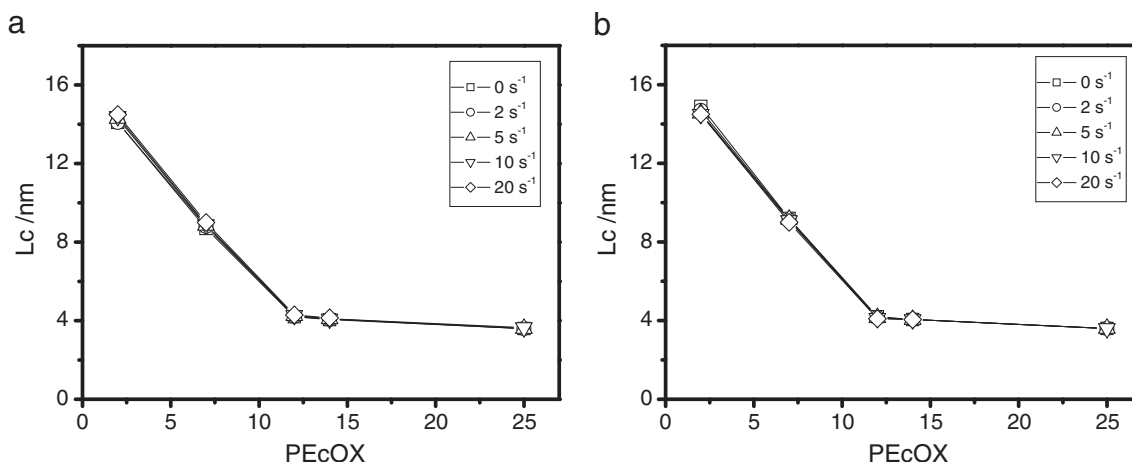


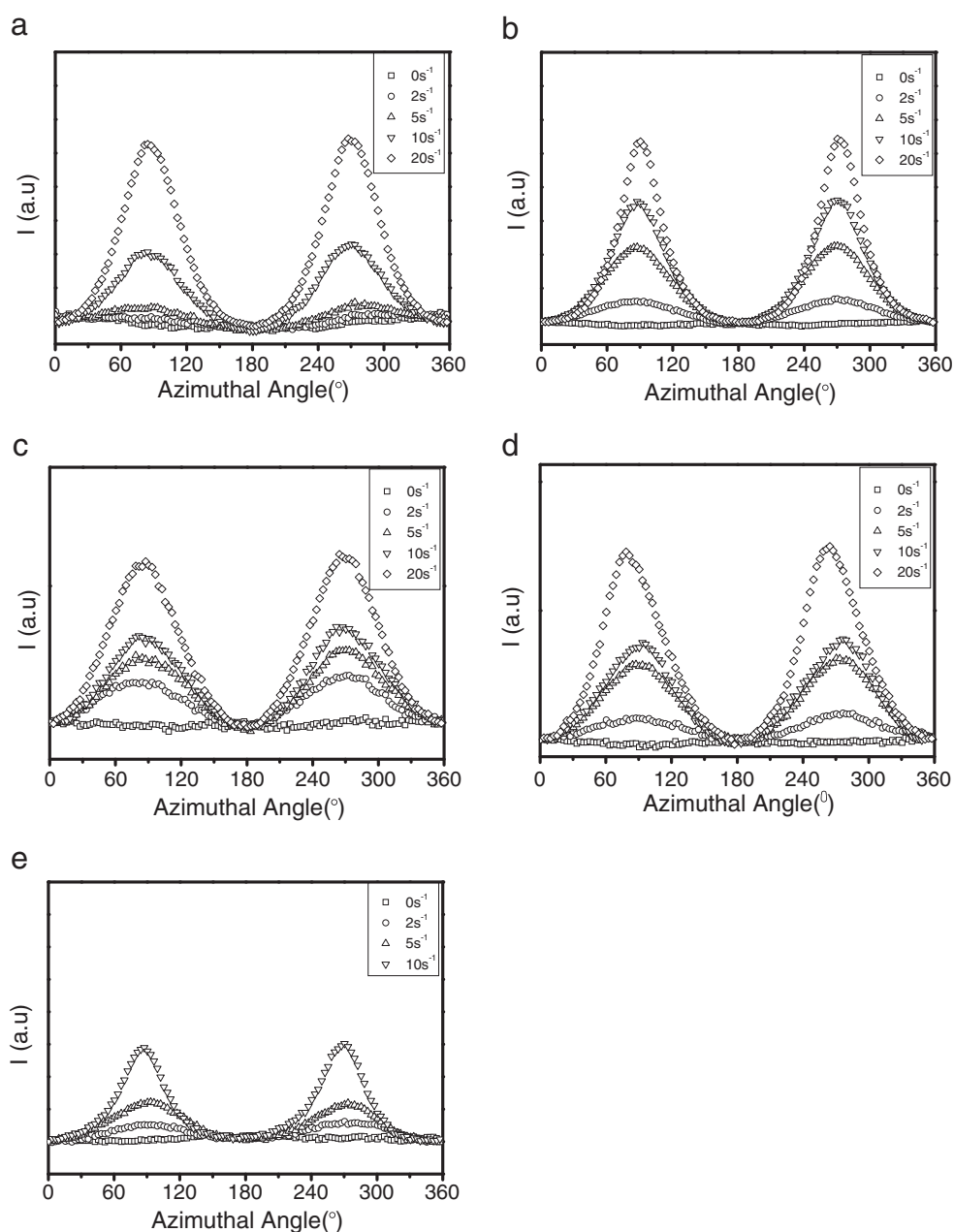
Fig. 9 Lamellar thickness (L_c) of PEcOx after isothermal crystallization at different shear rate. **a** along the meridian; **b** along the equator

as aforementioned L . With lower amount of branches the chain sequences mobility and flexibility for crystallization are higher and this can induce the backbone chain fully extension during initial crystallization process. It can be easily understood that L and L_c of PEcOx with low content of branches are large than that with high content of branches. It is worthy to noticing that when the branches content is higher than 12%, L and L_c remains essentially unchanged. For copolymers with low comonomer contents, the backbone chain length between branches is an important parameter which has a great influence on crystallization [34–36]. In the case of the copolymers with large amount of octene branches, the influence of chain length on

crystallization is likely to be weak because the increased friction which reduced mobility and the flexibility of sequences for crystallization has reached a maximum to a certain degree. Under such circumstances, long or short ethylene sequences are no longer important for progressively reducing mobility of chains and chain segments.

The orientation exponent f introduced by Hermans, is an often used method to value the degree of orientation [37, 38]. The appropriate application of the Hermans orientation function for SAXS analysis requires that the distribution of the lamellar normals must have an axial symmetry. The Hermans orientation function can be calculated according to the equation: $f = (3 \langle \cos^2 \varphi \rangle - 1) / 2$. It has the behavior

Fig. 10 Azimuthal intensity distribution of PEcOx after isothermal crystallization with the indicated shear rate: **a** PEcO2 with crystallization temperature 120 °C; **b** PEcO7 with crystallization temperature 105 °C; **c** PEcO12 with crystallization temperature 97 °C; **d** PEcO14 with crystallization temperature 92 °C; **e** PEcO25 with crystallization temperature 40 °C



that $f=1$ corresponds to perfect orientation in the $\varphi=0$ direction (All the lamellae are oriented with their normals perpendicular to the flow direction), $f=0$ for random orientation and $f=-1/2$ for perfect orientation of the normals parallel to the $\varphi=0$ direction (All the lamellae are oriented with their normals parallel to the flow direction). Figure 10 shows the azimuthal intensity distributions extracted from the SAXS patterns of the samples after isothermal crystallization under different shear rates; they show an axial symmetry of the distribution of the lamellar normals. Considering the various crystallization temperatures of PEcOx, it makes it difficult to compare the f values with each other. We normalized the orientation factor f to samples subject to the shear rate 20 s^{-1} . The values of the “orientation factor f ” as a function of shear rate for the ethyleneoctene copolymers are shown in Fig. 11. The results show an enhancement of f with increase of shear rate and, especially, increase rapidly when the shear rate was less than 10 s^{-1} . During initial crystallization, with temperature decreased and shear field imposed two polymer chains evolvement mechanisms involved, orientation and relaxation [39]. With crystallization progressing, the function of relaxation will gradually disappear and some oriented structure will be retained. Higher shear rate induces a higher degree of chain orientation and is in favor of a larger f for the lamellae accordingly. Here in Fig. 11 we found a interesting phenomenon that under the same shear conditions, the degree of lamellar orientation was enhanced with the increasing branches which was fully opposite to the shear influence on crystallite orientation (as is stated above). The increase in the content of branches makes the mobility capability of the crystalline polymer backbone chains decrease, i.e. when the observation focuses on the crystallite structure, the orientation degree decreased with the increasing of branching content. With the observation dimension increasing up to

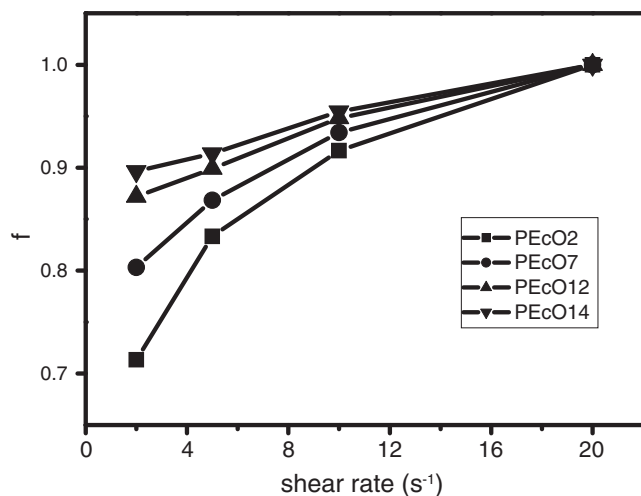


Fig. 11 Normalized lamellae orientation exponents f of the series of copolymers after isothermal crystallization as a function of shear rate

lamellae (tens of nm), we are convinced of a special structure which can be responsible for the increasing orientational degree with larger amount of branches content or stronger shear intensity. But what's the property of the special structure and what's its function during the crystallization process?

In recent years, some reports have suggested that there existed some transient structure during the process of initial crystallization [40–43]. Based on many SAXS observations and analysis, Strobl and coworkers proposed a mesophase concept which is a departure from the conventional one-step crystallization related to the nucleation and growth theory [44–46]. However, such an intermediate phase is very difficult to observe through all the conventional measurements because of the fact that it may only exist in a shell with a thickness below 100 nm on the front of a growing spherulite and or such a phase is more melt than crystal like. Even though that many results have been suggested to support the assumption, the theory still needs to be tested. We have investigated shear-induced sPP crystallization structure by WAXD and synchrotron SAXS techniques, and the obtained experimental data convinced us that there existed a stable mesophase before shear was imposed [47, 48]. In this paper we also find that shear can strongly influence the micro- and macrostructures of PEcOx and hence influence the crystallization process. All the experimental results suggest the existence of a mesomorphic phase passed through in the initial crystallization process. The transient mesophase structure was supposed to exist during the initial crystallization process even before shear composed. The mesomorphic phase is supposed to be composed of folded chains. Under shear, many polymer chains go through coil-stretch transition and align parallel to the shear direction which induces the formation of oriented intermediate phase. The orientation structure will be more or less retained under the competition between chain orientation and relaxation during crystallization. We are sure that the strong lamellar orientation is attributed to oriented mesomorphic phase existing in the initial crystallization in our experiment. The degree of lamellar orientation depends on the orientation of the mesophase structure. We know that with higher amount of branches polymer has smaller long period which means it is easier for mesophase to rotate and orient under shear condition. Once shear was imposed, the lamella orientation with higher amount of branches was more easier because of smaller lamellar size and more slowly relaxation of sheared polymer chains. Under the circumstance, the degree of lamellar orientation of polymer with larger branches content is higher with smaller branches content. For the existence of mesomorphic phase the shear effect on smaller observation scale, crystallite structure, weakens and the orientational degree correspondingly decreases. With the increasing amount of branches, the mobility of the polymer chains

decreases and consequently the influence of shear decreases and the degree of crystallite orientation decreases. On all accounts we have reason to believe that there exists mesophase structure during the initial crystallization stage before shear is imposed which determines the final crystallization structure.

Conclusions

Shear-induced crystallization structures of a series of Poly(ethylene-co-octene)s show that shear can greatly influence the crystallization process and determine the final crystallization structures. The long period, crystalline lamellae and the crystallite size have not been affected by shear but the orientation of crystalline lamellae and the crystallite are dependent on the shear rate, especially the orientation of lamellae. Some pre-ordered structure arraying regularly induces the occurrence of lamellar and crystallitic orientation. It can be concluded that there exists a mesomorphic structure in the initial crystallization even before the shearing which further develops into lamellae. The differences between the orientation of lamellae and crystallite in relation to octene content are elucidated. Based on all the analysis we have reason to believe that a relatively stable mesomorphic structure forms before the shearing and the final structure is determined by the evolution of the sheared mesophase.

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