

SIMULTANEOUS SAXS/WAXS/DSC STUDIES ON MICROSTRUCTURE OF CONVENTIONAL AND METALLOCENE-BASED ETHYLENE-BUTENE COPOLYMERS*

Jun-ting Xu**, Bo-tao Li and Zhi-qiang Fan

Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

Anthony J. Ryan

Chemistry Department, The University of Sheffield, Sheffield S3 7HF, UK

Abstract The fractions of one metallocene-based (mPE) and one conventional (znPE) ethylene-butene copolymer eluted at 80–82°C from temperature rising elution fractionation were selected for DSC and time-resolved small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) characterization. The DSC and WAXS results show that two crystal structures exist in both mPE and znPE: structure A with higher melting temperature and structure B with lower melting temperature. It was found that original znPE (s-znPE) contains more highly ordered structure A than original mPE (s-mPE) in spite of the higher comonomer content of znPE. Another structure C is also identified because of higher crystallinity measured by WAXS than by DSC and is attributed to the interfacial region. The SAXS data were analyzed with correlation function and two maxima were observed in s-mPE and s-znPE, in agreement with the conclusion of two crystal populations drawn from DSC and WAXS results. These two crystal populations have close long periods in s-mPE, but very different long periods in s-znPE. In contrast, freshly crystallized mPE and znPE (f-mPE and f-znPE) contain only a single crystal population with a broader distribution of long period

Keywords SAXS, WAXS, Microstructure, Metallocene, Ethylene-butene copolymer

INTRODUCTION

Ethylene- α -olefin copolymers usually have a complicated microstructure because of the coexistence of molecular weight distribution and inter- and intra-molecular composition distributions^[1–7]. These two distributions have an essential influence on polymer properties^[4, 8–18]. As a result, understanding the microstructure of ethylene- α -olefin copolymers is important and necessary.

Study of melting behavior after stepwise crystallization is the method most commonly used to evaluate inter- and intra-molecular composition distributions of ethylene- α -olefin copolymers^[2, 3]. The DSC melting peaks are believed to arise from the crystals of ethylene sequences with different lengths. Nevertheless, DSC gives only indirect information about the microstructure and the arrangement of the crystals but the lamellar thickness of the crystals cannot be obtained from DSC. Theoretically, such information can be readily revealed by SAXS^[19, 20]. However, under most of the crystallization conditions employed in the literature the SAXS result does not reflect the real sequence length distribution because of crystallization kinetics^[21]. For example, ethylene sequences with different lengths can co-crystallize in the same crystals and separation of the crystals formed by different sequences proceeds very slowly. Impingement of different crystals also retards the full growth of different

* This work was supported by the National Natural Science Foundation of China (Grant No. 29734144 and 59703002) and by the Special Funds for Major State Basic Research Projects (Grant No. G1999064803).

** Corresponding author: Jun-ting Xu (徐君庭), E-mail: xujt@ipsm.zju.edu.cn

Received February 25, 2003; Revised May 26, 2003; Accepted May 28, 2003

crystals. As a result, freshly crystallized and original samples, respectively, were used in the present work. Long-term storage permits the development of morphology formed by different sequences.

In this paper, one metallocene-based ethylene-butene copolymer (mPE) and one ethylene-butene copolymer prepared with a conventional Ziegler-Natta catalyst (znPE) were first fractionated by the preparative temperature rising elution fractionation (TREF) method and the fractions eluted in a narrow temperature range, in which intermolecular composition heterogeneity can be ignored, were selected for each sample. These two fractions under different crystallization conditions (freshly crystallized from the melt at a rate of 10 K/min and original) were characterized with time-resolved synchrotron SAXS/WAXS as well as DSC.

EXPERIMENTAL

Materials

The mPE and znPE copolymers were first fractionated with preparative temperature rising elution fractionation (TREF) method. The fractionation was described elsewhere^[22]. The fractions eluted between 80–82 °C were selected for structure characterization and time-resolved SAXS/WAXS experiments. The comonomer content, molecular weight and molecular weight distribution of these two fractions are listed in Table 1.

Table 1. Structural characteristics for mPE and znPE

	Comonomer content (mol%)	M_w	MWD
mPE	1.5	1.27×10^5	1.8
znPE	2.2	1.31×10^5	2.1

SAXS/WAXS/DSC

Simultaneous SAXS/WAXS/DSC experiments were carried out at beamline 8.2 of SRS at the Daresbury Laboratory, UK. The camera with a multiwire quadrant detector was located 3.5 m away from the sample. The samples were heated and cooled by a Linkam DSC at a rate of 10 K/min. Details of the experiments were described elsewhere^[23].

Data Processing

The observed scattering intensity $I(q)$ was Lorentz-corrected to yield the plot of $I(q)q^2$ versus scattering vector q . The Bragg spacing, *i.e.* the long period (L), was calculated from the maximum (q^*) in the plot of $I(q)q^2$ versus q by $L = 2\pi/q^*$. The invariant (Q) can be calculated by integration of Lorentz-corrected scattering intensity $I(q)q^2$ versus q from $q = 0$ to $q = \infty$. However, this need the extrapolation of $I(q)$ data to $q = 0$ and to $q = \infty$. Alternatively, only relative invariant (Q') was calculated according to following equation^[23]:

$$Q' = \int_{q_1}^{q_2} I(q)q^2 dq \quad (1)$$

where q_1 and q_2 are the q values of the first reliable data and the data where $I(q)q^2$ is constant, and equals 0.07 and 2.0 nm^{-1} , respectively.

Alternatively, the invariant can also be calculated from the volume fraction of spherulites (X_s), volume crystallinity within the lamellar stacks (ϕ_c) and the square of the electron density difference between the crystalline and amorphous phases ($\Delta\eta^2$)^[24]:

$$Q' = KX_s\phi_c(1 - \phi_c)\Delta\eta^2 \quad (2)$$

where K is a constant and $X_s \rightarrow 1$ for a well crystallized material (such as crystallized PE at room temperature).

The SAXS data was also analyzed with a one-dimensional correlation function (γ_1) based on an ideal lamellar morphology using a CORFUNC program provided by CCP13 at Daresbury. In this program, the SAXS data were first extrapolated to $q = 0$ according to Guiner's law and to $q = \infty$ using a damped Porod function, respectively, then a cosine Fourier transformation was performed^[23].

$$\gamma_1(r) = \frac{1}{Q} \int_0^\infty I(q) q^2 \cos(qr) dq \quad (3)$$

Figure 1 is a typical correlation function of a crystalline polymer. From the correlation function some useful parameters such as long period (L), lamellar thickness of crystalline phase (L_c), and crystallinity within the lamellar stacks (ϕ_c) can be determined, as indicated in Fig. 1^[25, 26].

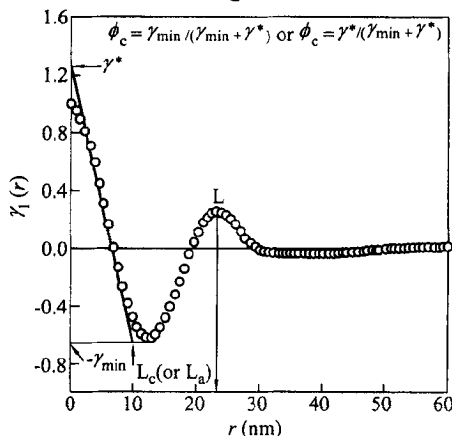


Fig. 1 Typical correlation function for crystalline polymer with the values of L , L_c and ϕ_c are indicated

In WAXS, weight fraction crystallinity (X_c) is calculated from the area of amorphous peak (A_a) and the area of crystalline peaks (A_c):

$$X_c = A_c / (A_c + A_a) \quad (4)$$

A_c and A_a were determined by a XFIT program designed by CCP13.

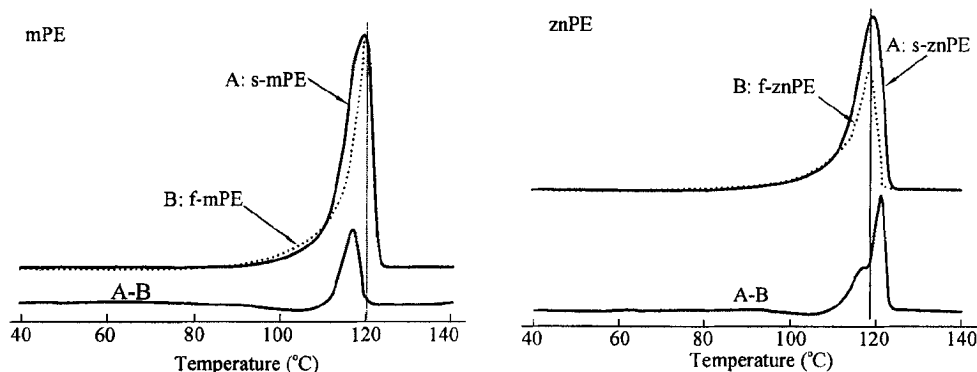


Fig. 2 DSC melting curves of original and freshly crystallized samples and the difference between these two curves a) mPE; b) znPE

RESULTS AND DISCUSSION

DSC Results

Figure 2 shows the DSC melting curves of the original (s-mPE, s-znPE) and freshly crystallized samples (f-mPE, f-znPE) and the difference between these two curves. It was found that s-mPE and f-mPE have the same melting temperatures (T_m^P) at 120°C, while the melting temperatures of s-znPE and f-znPE are slightly different, being 119.5°C and 118.5°C, respectively. This shows that s-mPE and s-znPE have similar T_m^P . However, one should

bear in mind that the comonomer content in mPE is lower than that in znPE. As a result, comonomer units reduce the melting temperature more efficiently in mPE, which has been reported by different authors. One can also see from Fig. 2(a) that the melting traces can be divided into two zones by a vertical line at T_m^P . After T_m^P the melting traces of s-mPE and f-mPE are overlapped, but before T_m^P the area under the melting trace of s-mPE is larger than that of f-mPE. Similarly, the melting traces of znPE are also divided into two zones, but s-znPE has larger areas under the melting trace than f-znPE both before and after T_m^P (Fig. 2b).

WAXS Results

The WAXS patterns of s-mPE, f-mPE, s-znPE and f-znPE during heating are shown in Fig. 3 and the variations of weight fraction crystallinity (X_c) with temperature are depicted in Fig. 4. It can be seen from Fig. 4 that original samples have higher crystallinity than freshly crystallized sample at room temperature. Such a difference is more remarkable for znPE. A decrease in crystallinity is observed for all samples when they are heated from room temperature to 60°C, though no melting peak is detected by DSC in this temperature range. Moreover, we notice that crystallinity at room temperature calculated from the fusion enthalpy in DSC is smaller than that from WAXS. Therefore, a structure, which cannot be detected by DSC but can be detected by WAXS, also contributes to crystallinity. Considering the lower melting temperature, such a structure is least ordered and may be produced by very short sequence. The difference in crystallinity measured by DSC and WAXS has been reported by other authors and it is generally attributed to a partially ordered interfacial region, which lies between the amorphous region and the ordered crystalline region^[27–29]. Above 60°C, the change of crystallinity with temperature can be divided into two zones. The first one is from 60°C to 120°C, in which crystallinity decreases relatively slower with increasing temperature. The second zone is from 120°C to 125°C. In such a narrow temperature range, crystallinity decreases drastically with temperature. These two zones correspond to those classified in DSC. Comparing Fig. 4(a) and (b), we notice that the stepwise change of crystallinity is more evident for znPE.

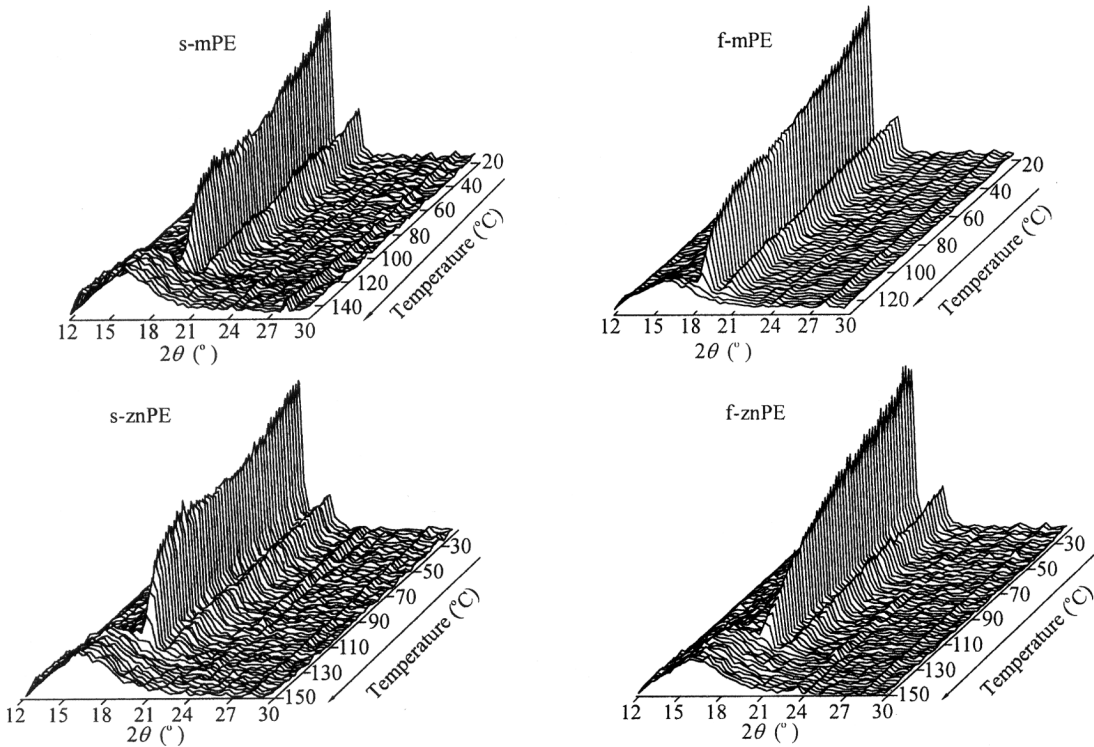


Fig. 3 WAXS patterns for s-mPE, f-mPE, s-znPE and f-znPE

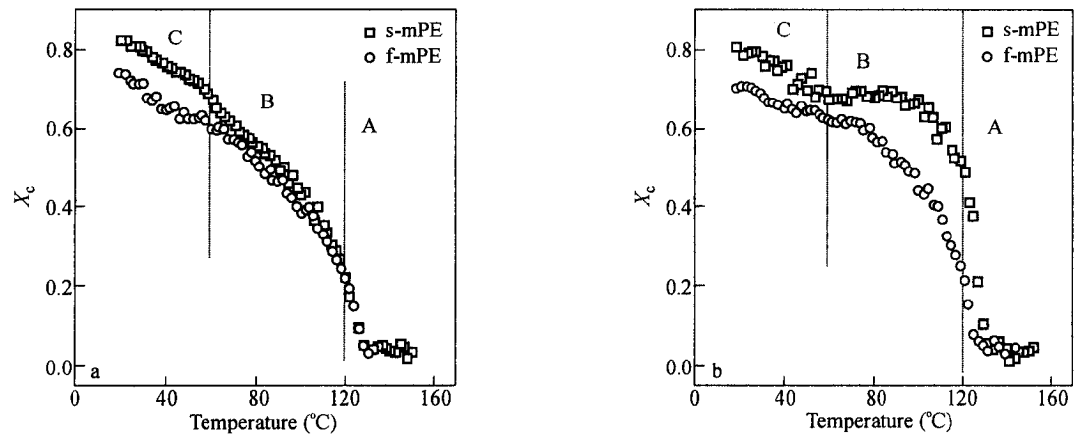


Fig. 4 Variation of weight fraction crystallinity X_c with melting temperature
a) mPE; b) znPE. The melting temperature ranges of different structures are indicated

The DSC and time-resolved WAXS results reveal that there exist three types of ordered structures in both mPE and znPE: The highly ordered structure (A) melting between 120°C and 125°C; the intermediately ordered structure (B) melting between 60°C and 120°C (The broad melting temperature range means that there still exist a variety of orderliness in this type structure.); and the least ordered structure (C) which melts between room temperature and 60°C. The changes of X_c originating from melting of these three different structures are listed in Table 2. The data show that the main difference between s-znPE and s-mPE lies in the percentage of structure A and B. More highly ordered structure A is found in s-znPE, though more comonomer units are enchain in znPE. For f-mPE and f-znPE the difference in the distribution of these three types of structure is very small.

Table 2. Distributions of different structures

Sample	Structure		
	A	B	C
s-mPE	0.23→0 (0.23)	0.68→0.23 (0.45)	0.82→0.68 (0.14)
f-mPE	0.23→0 (0.23)	0.60→0.23 (0.37)	0.74→0.60 (0.14)
s-znPE	0.50→0 (0.50)	0.68→0.50 (0.18)	0.81→0.68 (0.13)
f-znPE	0.26→0 (0.26)	0.61→0.26 (0.35)	0.71→0.61 (0.10)

SAXS Results

The SAXS profiles for s-mPE, f-mPE, s-znPE and f-znPE at different temperatures are shown in Fig. 5. It can be observed that freshly crystallized samples have stronger SAXS peaks than corresponding original samples. This is because original samples have higher crystallinity and the volume fraction crystallinity (ϕ_c) of all the samples exceeds 0.50. One can see from Eq. (2) that the invariant Q has a maximum value at $\phi_c = 0.5$ and it increases with the decrease in crystallinity when $\phi_c > 0.5$. As shown in Fig. 5, at lower temperature when ϕ_c is larger than 0.5, the intensity of SAXS peaks increases with temperature. Figure 6 shows the change of long period calculated from Lorentz-corrected SAXS peaks with temperature. It is found that the long period basically remains constant when temperature is kept between room temperature and 60°C, regardless of samples and crystallization conditions. This suggests that the melting of the interfacial region has no effect on the long period. When the temperature exceeds 60°C, the long period increases with temperature because thinner crystals melt first at lower temperature^[23]. However, freshly crystallized samples exhibit a faster change in the long period with temperature than the original samples. Comparing the long periods of mPE and znPE, we can see that they are remarkably different at the same temperature, though these two samples have similar T_m^P . The long period for s-

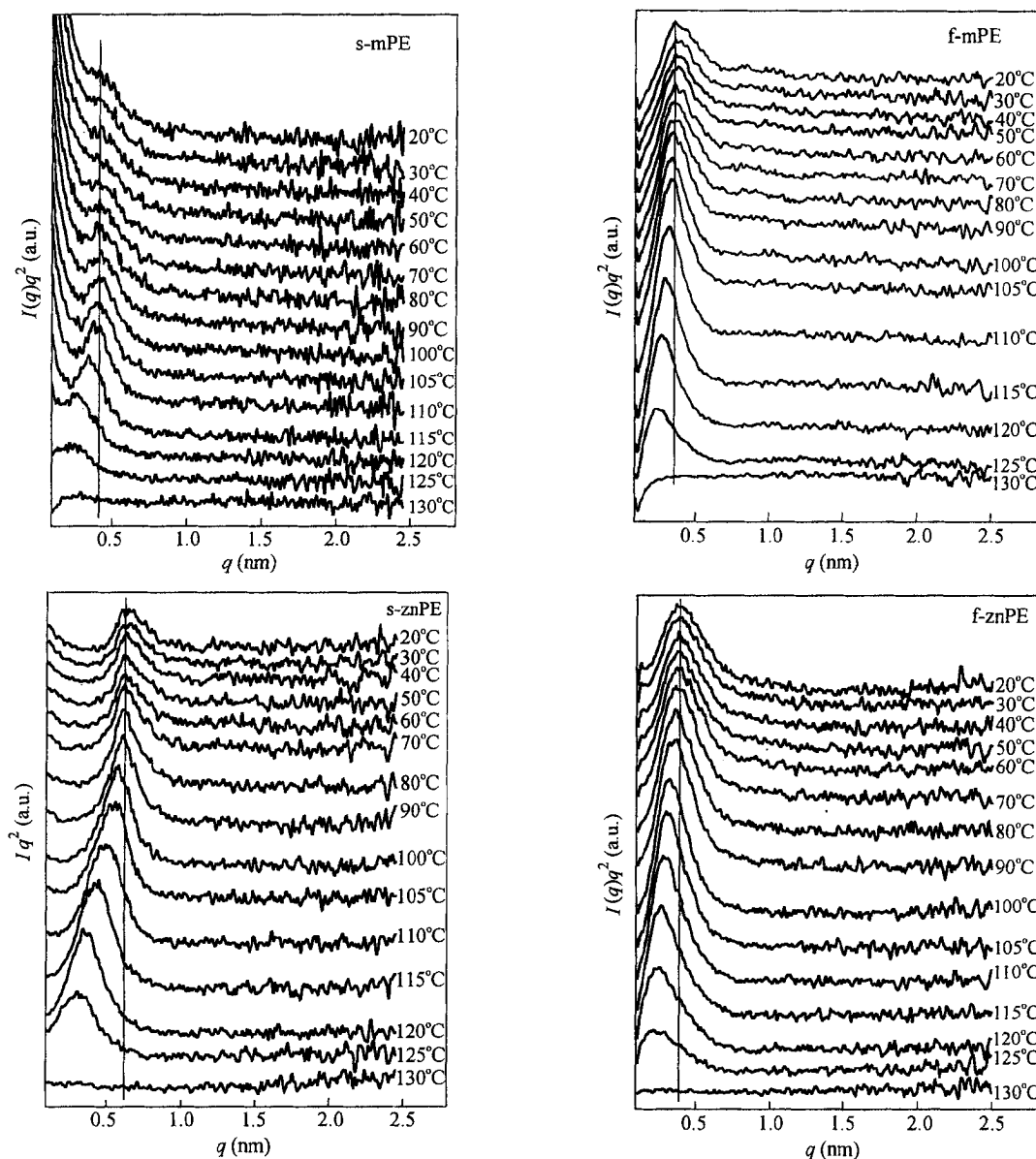


Fig. 5 SAXS profiles for s-mPE, f-mPE, s-znPE and f-znPE

mPE is about 15 nm at room temperature and is only 9 nm for s-znPE. On the other hand, f-mPE and f-znPE have a similar long period at lower temperature, *i.e.* 16.4 nm and 16 nm, respectively, at room temperature. At higher temperature, f-mPE and f-znPE have different long periods because f-mPE has higher T_m^P . The larger long period of s-mPE than s-znPE implies that s-mPE contains more highly ordered structure A. This result contradicts that obtained by WAXS and DSC. Analysis using correlation function can give an explanation of such an apparent discrepancy. The correlation functions of s-mPE, f-mPE, s-znPE and f-znPE at different temperatures are illustrated in Fig. 7. The maximum in the correlation function corresponds to the long period of lamellar stacks. For s-mPE the maximum in correlation functions is not evident below 60°C. Above 60°C a maximum is observed at 12 nm, but another maximum also appears at 15 nm as a shoulder. The SAXS profiles only reflect the crystal population of $L = 15$ nm. Two maxima can also be observed in the correlation functions of s-znPE, even at temperatures below 60°C. However, these two maxima are well separated, which are located at 9 nm

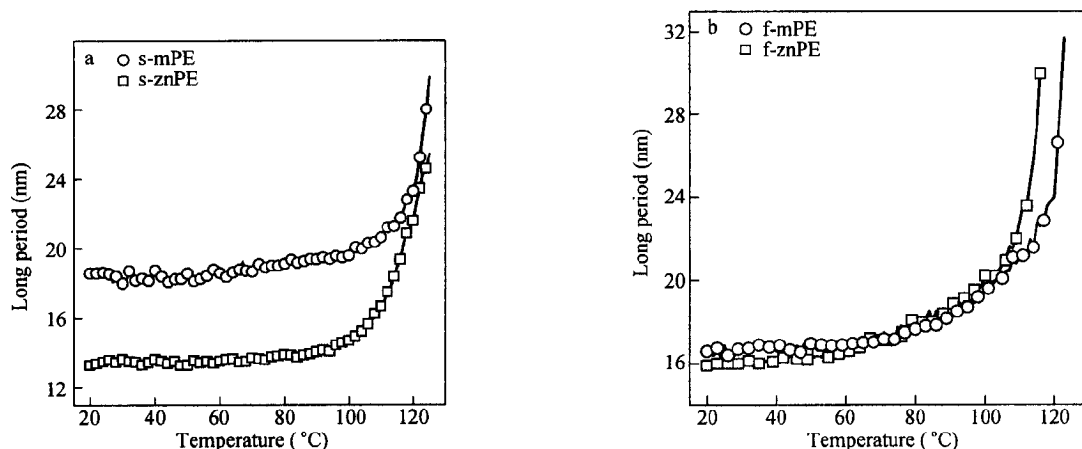


Fig. 6 Change of the long period L with temperature
a) s-mPE and s-znPE; b) f-mPE and f-znPE

and 18 nm, respectively, and the SAXS profiles of s-znPE only reflect the former one. As a result, the correlation function shows that there are two crystal populations in both s-mPE and s-znPE. The crystals with shorter long period may correspond to the intermediately ordered structure and the crystals with larger long period correspond to the highly ordered structure A observed in WAXS and DSC. The differences between the long periods of crystal populations indicate that these two crystal populations are similar in s-mPE but quite different in s-znPE. On the other hand, for the freshly crystallized samples only a single maximum is observed in both f-mPE and f-znPE at most temperatures. This suggests that the two crystal populations are merged into one due to co-crystallization at a fast cooling rate. Since the long period changes more rapidly with temperature in the freshly crystallized samples than that in the original samples, the distribution of long period of the lamellar stacks in the freshly crystallized samples is broader than that of any single crystal population corresponding to the original samples. The long period of f-mPE is about 16 nm, very close to that of the second crystal population in s-mPE, indicating that the second crystal population becomes predominant in f-mPE. This result is in agreement with that of DSC. We observed that the contents of highly ordered structure A are similar in s-mPE and f-mPE, but the intermediately ordered structure B becomes less in f-mPE. The long period of f-znPE determined from the correlation function is 15.5 nm at 20°C, which lies between the long periods of the two crystal populations in s-znPE.

We noticed that multiple maxima are also observed in f-mPE and f-znPE above 110°C. This may be due to the AC-AC structure evolution model in crystallization of ethylene copolymers, as described in the literature^[21]. Moreover, the vibration at high r values in the correlation functions can be attributed to the influence of beamstop on the data.

CONCLUSIONS

Three types of ordered structures can be identified by DSC and time-resolved WAXS in both mPE and znPE: the highly ordered structure A melting between 120°C and 125°C, the intermediately ordered structure B melting between 60°C and 120°C and the least ordered structure C melting between room temperature and 60°C. Structure C is attributed to the interfacial phase and the melting of this structure has no effect on the long period, whereas structures A and B are ascribed to different crystals. Crystallization conditions greatly influence the crystal structures and their distributions. Time-resolved SAXS reveals that there are two crystal populations with different long periods in original mPE and znPE. The difference in the long periods of these two crystal populations is small for s-mPE, but very large for s-znPE, indicating a broader composition distribution of znPE.

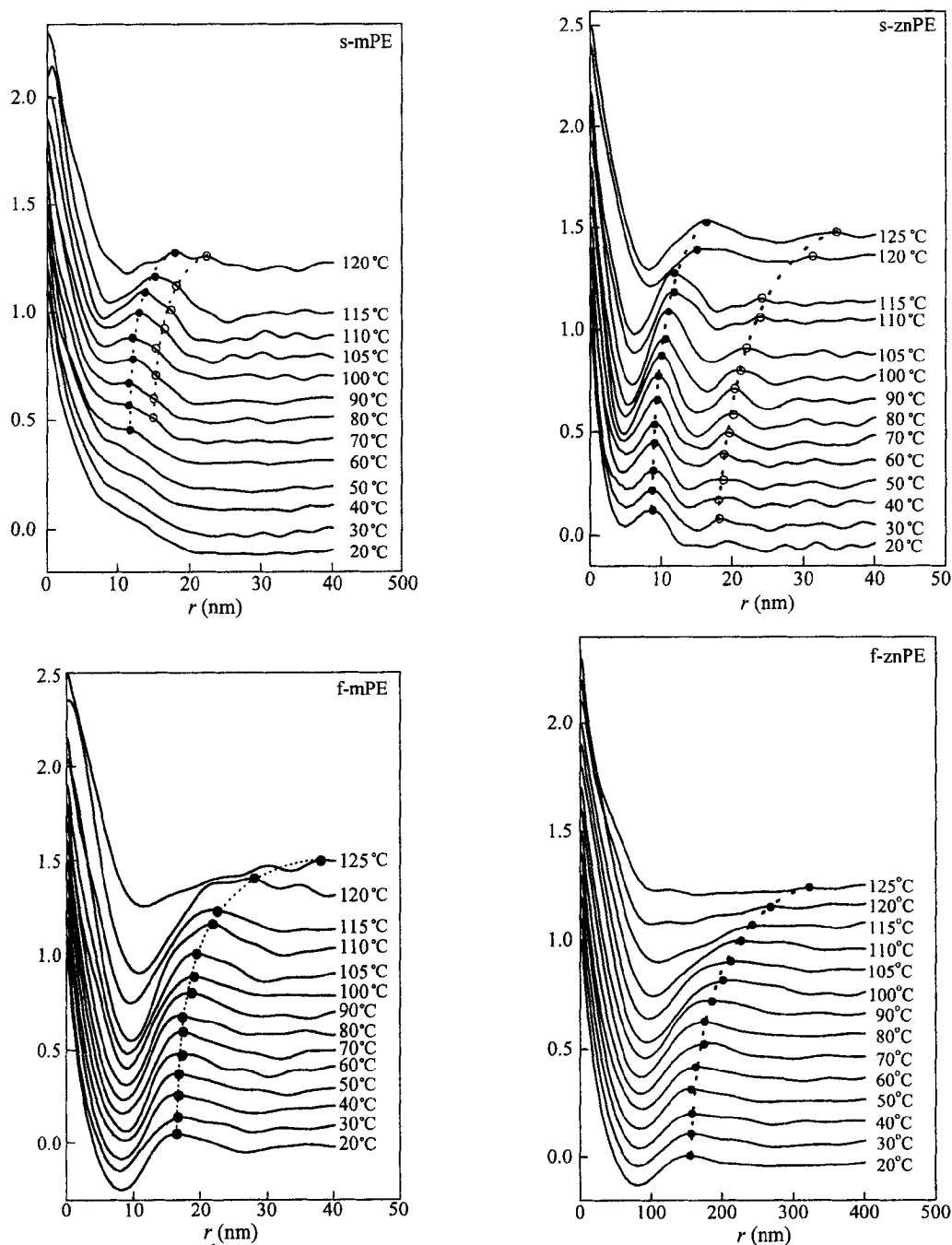


Fig. 7 Correlation functions (CF) for s-mPE, f-mPE, s-znPE and f-znPE at different temperatures. The solid and open circles indicate the maxima. For the purpose of clarity the curves are displaced and the displacement among different curves can be estimated from $CF = 1.0$ at $r = 0$ for all curves.

For the freshly crystallized samples, these two crystal populations are merged into a single population with broader long period distribution and the long periods and the distribution of different structures are similar for mPE and znPE.

REFERENCES

- 1 Kakugo, M., Miyatake, T. and Mizunuma, K., *Macromolecules*, 1991, 24: 1469
- 2 Starck, P., *Polym. Int.*, 1996, 40: 111
- 3 Hsieh, E.T., Tso, C.C., Byers, J.D., Johnson, T.W., Fu, Q. and Cheng, S.Z.D., *J. Macromol. Sci.-Phys.*, 1997, 36: 615
- 4 Xu, J.T., Xu, X.R., Chen, L.S. and Feng, L.X., *J. Mater. Sci. Lett.*, 2000, 19: 1541
- 5 Xu, J.T., Xu, X.R. and Feng, L.X., *Eur. Polym. J.*, 2000, 36: 685
- 6 Xu, J.T., Xu, X.R., Feng, L.X., Chen, L.S. and Chen, W., *Macromol. Chem. Phys.*, 2001, 202: 1524
- 7 Fu, Q., Chiu, F.C., He, T.B., Liu, J.P. and Hsieh, E.T., *Macromol. Chem. Phys.*, 2001, 202: 927
- 8 Gaucher-Miri, V., Elkoun, S. and Seguela, R., *Polym. Eng. Sci.*, 1997, 37: 1672
- 9 Fu, Q., Chiu, F.C., McCreight, K.W., Guo, M.M., Tseng, W.W., Cheng, S.Z.D., Keating, M.Y., Hsieh, E.T. and DesLauriers, P.J., *J. Macromol. Sci.-Phys.*, 1997, B36: 41
- 10 Mathot, V.B.F., Scherrenberg, R.L. and Pijpers, T.F.J., *Polymer*, 1998, 39: 4541
- 11 Gelfer, M.Y. and Winter, H.H., *Macromolecules*, 1999, 32: 8974
- 12 Nitta, K.H. and Takayanagi, M., *J. Polym. Sci. Polym. Phys.*, 2000, 38: 1037
- 13 Vanden Eynde, S., Mathot, V.B.F., Hohne, G.W.H., Schawe, J.W.K. and Reynaers, H., *Polymer*, 2000, 41: 3411
- 14 Xu, X.R., Xu, J.T., Feng, L.X. and Chen, W., *J. Appl. Polym. Sci.*, 2000, 77: 1709
- 15 Xu, X.R., Xu, J.T., Chen, L.S., Liu, R.W. and Feng, L.X., *J. Appl. Polym. Sci.*, 2001, 80: 123
- 16 Xu, J.T., Xu, X.R., Chen, L.S., Feng, L.X. and Chen, W., *Polymer*, 2001, 42: 3867
- 17 Xu, X.R., Xu, J.T. and Feng, L.X., *Chin. J. Polym. Sci.*, 2002, 20: 473
- 18 Xu, X.R., Xu, J.T. and Feng, L.X., *Polym. Int.*, 2002, 51: 458
- 19 Mathot, V.B.F., Scherrenberg, R.L., Pijpers, M.F.J. and Bras, W., *J. Therm. Anal.*, 1996, 46: 681
- 20 Goderis, B., Reynaers, H., Koch, M.H.J. and Mathot, V.B.F., *J. Polym. Sci. Polym. Phys.*, 1999, 37: 1715
- 21 Goderis, B., Reynaers, H. and Koch, M.H.J., *Macromolecules*, 2002, 35: 5840
- 22 Xu, J.T. and Feng, L.X., *Eur. Polym. J.*, 2000, 36: 867
- 23 Ryan, A.J., Stanford, J.L., Bras, W. and Nye, T.M.W., *Polymer*, 1997, 38: 759
- 24 Glatter, O. and Kratky, O., "Small Angle X-ray Scattering", Academic Press, London, 1982
- 25 Strobl, G.R. and Schneider, M.J., *J. Polym. Sci. Polym. Phys.*, 1980, 18: 1343
- 26 Strobl, G.R. and Schneider, M.J. and Voigt-Martin, I.G., *J. Polym. Sci. Polym. Phys.*, 1980, 18: 1361
- 27 Peacock, A.J. and Mandelkern, L., *J. Polym. Sci. Polym. Phys.*, 1990, 28: 1917
- 28 Mandelkern, L., *Accounts Chem. Res.*, 1990, 23: 380
- 29 Mandelkern, L., *Polym. J.*, 1985, 17: 337