

STUDIES ON THE NATURE OF THE MACROMOLECULAR CONDENSED STATE OF "NASCENT" ULTRA HIGH MOLAR MASS POLYETHYLENE*

Zhong-yong Fan^a, Qiang Lan^a, Hai-shan Bu^a, Li-heng Wu^b, Lin Sun^b, Ren-yuan Qian^{c**},
Shou-xi Chen^c, Yong-feng Men^{d***} and Bing-zheng Jiang^d

^a Department of Materials Science, Fudan University, Shanghai 200433

^b China Textile Academy, PO Box 651, Beijing 100025

^c Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

^d Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

Abstract Ultra high molar mass polyethylene (UHPE) powder as polymerized in a slurry process has been studied, in its nascent state, after recrystallization on rapid cooling from the melt and after hot compression molding to a film, by DSC, effect of annealing the recrystallized specimen at 120~130°C, morphology by polarizing optical microscopy and small angle X-ray scattering. Based on the experimental results obtained the macromolecular condensed state of the nascent UHPE powder is a rare case of a multi-chain condensed state of non-interpenetrating chains, involving interlaced extended chain crystalline layers and relaxed parallel chain amorphous layers. On melting, a nematic rubbery state of nanometer size domain resulted. The nematic-isotropic transition temperature was judged from literature data to be at least 220°C, possibly higher than 300°C, the exact temperature is however not sure because of chain degradation at such high temperatures. The recrystallization process from the melt is a crystallization from a nematic rubbery state. The drop of remelting peak temperature by 10 K of the specimen recrystallized from its melt as compared to the nascent state has its origin in the decrease both of the crystalline chain stem length and of the degree of crystallinity. The remelting peak temperature could be returned close to that of the nascent state by annealing at 120~130°C.

Keyword Ultra high molar mass polyethylene, Recrystallization, Remelting, Annealing, Nematic state

INTRODUCTION

Ultra-high molar mass polyethylene (UHPE) is produced with a heterogeneous Ziegler-Natta catalyst in a slurry process with a hydrocarbon diluent, which is a solvent for the growing PE chain only at low molar masses, while the growing chain at higher molar mass precipitates and crystallizes from the diluent. The fine powdered material separated from the reaction slurry, known as "nascent" UHPE, shows a very high molar mass of a few millions, a high degree of crystallinity over 70% and a melting peak temperature over 140°C by differential scanning calorimetry (DSC), while an ordinary linear polyethylene (HDPE) of $M < 10^6$ has crystallinities $< 50\%$ and a DSC melting peak around 134°C. The term nascent refers to the fact that after the powder as polymerized is subjected to a DSC heating up run over its melting point followed by a cooling scan to below 50°C, showing a crystallization exothermal peak around 120°C, a second heating up run will show a melting endothermic peak around 134°C, that is a 10 K drop of the melting peak temperature from that of the nascent state. Based on the high melting temperature^[1] and significant anisotropic light scattering^[2] of the nascent UHPE a fully extended chain model has been proposed for the macromolecular condensed state of nascent UHPE. The drop of melting

* This work was supported by the National Key Projects for Fundamental Research — "Macromolecular Condensed State", Ministry of Science and Technology, China

** Corresponding author: Ren-yuan Qian (钱人元), E-mail: qian@public.bta.net.cn

*** At present: Faculty of Physics, University of Freiburg

Received April 5, 2000

temperature of recrystallized UHPE was interpreted as conversion of a fully extended chain to a folded chain lamella on recrystallization. A possible mechanism of extended chain crystallization succeeding polymerization of gaseous ethylene on a Ziegler-Natta catalyst was suggested by Wegner *et al.*^[3], and studied in more detail by Smith *et al.*^[4] who showed that the macromolecular condensed state depended very much on the temperature of polymerization relative to the dissolution temperature of crystalline PE in the diluent used for polymerization.

In this paper more experimental results on the effect of annealing of recrystallized UHPE and the one-dimensional electron density correlation function of the nascent UHPE as determined from small angle X-ray scattering (SAXS) are presented. A refined understanding of the nature of the molecular chain condensed state in nascent UHPE has been attained taking into consideration of more recent experimental results to have appeared in the literature^[5-10].

EXPERIMENTAL

Samples

Two samples of nascent UHPE were used in this investigation. Sample A was prepared in the laboratory by Shangan Lin of Zhongshan University, Guangzhou, having $M_n = 1.2 \times 10^6$ and DSC melting peak temperature $T_m = 140.4^\circ\text{C}$ (ca. 3 mg sample, 10 K/min). The other sample B was Hoechst Hostalen GUR 412, $M_n = 4 \times 10^6$, containing a corrosion inhibitor^[6], and $T_m = 142.3^\circ\text{C}$ (ca. 5 mg sample, 10 K/min). Because of the effect of heat conduction in the dynamic state of temperature scanning in a DSC run and the heterogeneity in the structure of the crystalline state and the melt, the value of the melting peak T_m depends appreciably on the temperature scanning rate^[5, 7] and the amount of sample used.

DSC

The differential scanning calorimeters used were a DuPont TA-2000 DSC 910 (for the sample A, 3 mg sample per run) and a Perkin-Elmer Model 2-C system with data station (for the sample B, ≤ 5 mg sample per run). Temperature scanning rate was 10 K/min in all cases. The temperature of the endothermic peak in a heating up run was taken as T_m .

SAXS

Small angle X-ray scattering measurements were carried out at the University of Freiburg. The sample in a brass sample holder was mounted in an evacuated Kratky camera of PAAR, Graz, Austria, during SAXS experiments. A sealed X-ray tube with Cu anode and a Siemens Kristalloflex 710H generator were used. A primary monochromator selects the wavelength of CuK_α radiation, $\lambda = 0.154$ nm. The accessible range of scattering vector $q = (4\pi/\lambda) \sin(\theta/2)$ in nm^{-1} was $0.1 < q < 5$, θ being the scattering angle. The scattered intensity was recorded using a scintillation counter in a step scanning mode. Due to the beam geometry of the Kratky camera, the scattered intensity at one angle contains contributions of a certain range of scattering vectors. Therefore the scattering intensity data were desmeared using the standard procedure^[11]. The intensity data were put on the absolute scale using the moving slit device (PAAR) to determine the flux of the incident beam. SAXS data treatment was based on the one-dimensional electron density correlation function after Strobl^[12].

Morphology

Morphology observations were made by polarizing optical microscopy (POM) using an Olympus Model BH-2 with a Mettler FP-52 type hot stage.

RESULTS AND DISCUSSION

Effect of Annealing on the Remelting Behavior of the Nascent UHPE Powder after Melting and Subsequent Recrystallization on Cooling

For each run, 3 mg of the sample A was melted at 160°C for 5 min and then quenched in liquid nitrogen. The quenched sample was annealed in a constant temperature metal box at 123°C for various times up to 138 h. After annealing the sample was cooled to room temperature and heating up DSC curves were recorded as shown in

Fig. 1. The sample melted and quenched without annealing shows a single endothermic peak at 130°C. The annealed samples show two endothermic peaks, a low temperature melting peak at or below 130°C alongside a high temperature melting peak which increased in T_m with increasing annealing time as shown in Figs. 1 and 2. The value of T_m after 100 h annealing at 123°C approached the T_m of the nascent state (140.4°C). Annealing at 121.2°C showed the similar behavior. Nascent UHPE after melt recrystallization followed by annealing at 131–132°C to show multiple melting peaks on subsequent DSC run was also observed by Wang and Salovey^[6]. Similar experiments were performed with sample B, which had been heated to 160°C for 5 min and then quenched in ice-water. Annealing at 130°C for various times increased T_m from 132.7 (not annealed) to 139°C in 170 h, not yet reaching the limiting value, and slightly lower than 142.3°C for the nascent state. After annealing the melting endothermic peak remained single, the width of which became significantly narrower. An increase of ΔH_m from 150 J/g (not annealed) to 195 J/g (annealed) was observed, corresponding to a change in crystallinity X_c from 51% to 67%, approaching the value $\Delta H_m = 202$ J/g or $X_c = 69\%$ for the nascent state, if $\Delta H_m = 293$ J/g is taken for a fully crystallized PE^[13, 14]. Apparently the recrystallized sample, after annealing at T_a around 120°C and quenching, gives double melting peaks on the heating up DSC curve, while those samples annealed at 130°C give a single melting peak. It is clear that annealing the recrystallized UHPE at a temperature $T_a = 120\sim 130^\circ\text{C}$ for a sufficient time can return the molecular chain condensed state back to the nascent state. Similar annealing process for a HDPE sample at $T_a = 105^\circ\text{C}$, which was found to be the most effective annealing temperature in the sense of increasing T_m , for 120 h increased T_m from 127.9 to 131.3°C, an increase of only 3.4 K. This signifies that melting of the nascent UHPE at 160°C for 5 min will not bring the melt into a state of interpenetrated chains corresponding to an ordinary PE melt.

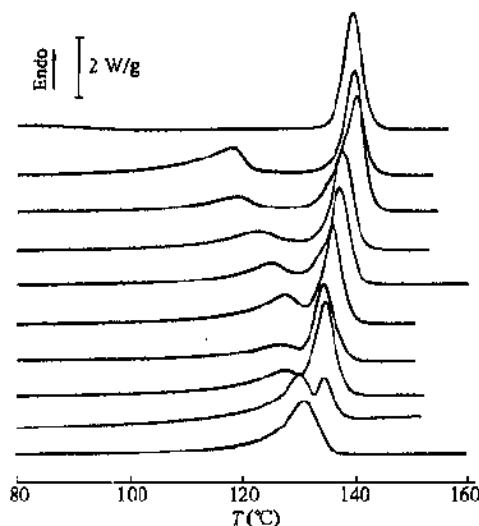


Fig. 1. DSC curves of the sample A after being melted at 160°C for 5 min and then the quenched sample annealed at 123°C for up to 138 h and quenched. Curves from bottom to top for annealing times 0, 0.17, 0.5, 1.5, 3.5, 7.5, 24, 48, 72 and 138 h, respectively.

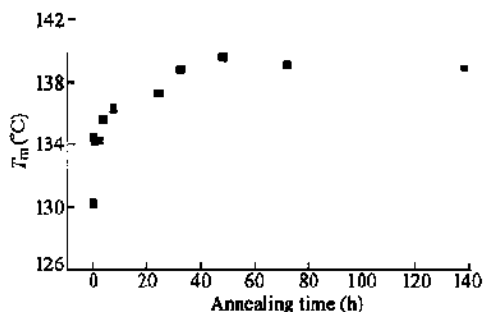


Fig. 2. Effect of annealing at 123°C on the DSC melting peak temperature T_m .

When the nascent UHPE sample B in the capsule of the DSC instrument is heated up at 10 K/min to temperatures 170°, or 160°, or 150°C each for 5 min and then recrystallized by rapid cooling at 160 K/min to room temperature, the values of T_m (132.5°C) and ΔH_m (150 J/g) on remelting are the same, independent of the melting temperature before recrystallization. Even when the sample was subjected to melting at 200°C for 5 min followed by rapid cooling, the remelting behavior remained the same. In this case 0.5% of an antioxidant had been mixed with the UHPE powder. The experimental results are summarized in Table 1.

Table 1. Remelting behavior of UHPE sample B melted and recrystallized on rapid cooling

Sample, melting condition before recrystallization	T_m (°C)	ΔH_m (J/g)	X_c (%)
Nascent powder	142.3	202	65
150°C, 5 min	132.4	150	51
160°C, 5 min	132.7	150	51
170°C, 5 min	132.4	151	52
200°C, 5 min	133.3	150	51

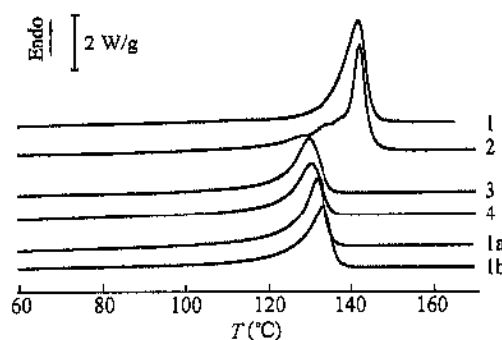
Effect of Compression Molding the Nascent UHPE Powder into a Film on the Remelting Behavior

Three grams of the UHPE sample B was uniformly spread onto the platen of a rubber vulcanization press and the press was heated to a given temperature and held at a pressure of 15 MPa for a given time, and then the compression molded film was quenched in ice-water. In the case of molding at 200°C 0.5% of an antioxidant was added to the nascent UHPE powder. The remelting behavior of these compression molded films is listed in Table 2.

Table 2. Remelting behavior of hot compression molded films of UHPE sample B

Condition of compression molding	T_m (°C)	ΔH_m (J/g)	X_c (%)
130°C, 120 min	142.6	191	65
170°C, 30 min	130.3	130	44
200°C, 18 min	131.6	134	46

The DSC curves are shown in Fig. 3. The results clearly indicate that when UHPE nascent powder was compression molded at 130°C, the molecular chain condensed state remains the same as in the nascent powder. This is in accord with finding of Wang, Li and Salovey^[7] that UHPE film compression molded at 140°C retained the melting behavior of the nascent powder. However, when the nascent powder is compression molded at 170°C and recrystallized on rapid cooling, the resulting film has a different molecular chain condensed state from the nascent state, showing a significant drop of T_m .

**Fig. 3** DSC curves of the compression molded films of the sample B

- 1) Nascent powder
- 1(a) Nascent powder after melted at 170°C, 5 min and quenched
- 1(b) Nascent powder after melted at 200°C, 5 min and quenched
- 2) Compression molded at 130°C, 120 min
- 3) Compression molded at 170°C, 30 min
- 4) Compression molded at 200°C, 18 min

A Tentative Interpretation of the Experimental Results

The high T_m of the nascent UHPE powder has been attributed to a fully extended chain conformation^[1, 2]. From the SAXS data of the sample B a long period $L = 41$ nm was deduced from the peak position of the $j(s)s^2$ versus s plot shown in Fig. 4, where $j(s)$ is the scattered intensity as a function of s , where $s = q/2\pi$, q being the scattering

vector. The one-dimensional electron density correlation function $K(z)$ obtained is shown in Fig. 5, K being in units of $(\text{electrons}/\text{nm}^3)^2$. The initial straight part of $K(z)$ is limited to a small range of z values near the origin, which cuts the ordinate rather sharply, indicating negligible transition zone of the lamellar surfaces, followed by pronounced curvature of $K(z)$. This probably means a non-uniformity in the crystalline chain stem length. The nearest neighbour correlation is weak but the most probable long period could be evaluated from the peak position of $K(z)$ in agreement with $L = 41$ nm obtained above. The diffuseness of the peak also indicates a broad distribution of long periods. No "base line" was observed. The scattering invariant Q , which is $K(z = 0)$, evaluated from Fig. 5 is 304 $(\text{electrons}/\text{nm}^3)^2$. As $Q = X_c X_a (\eta_c - \eta_a)^2$, where $(\eta_c - \eta_a)$ is the electron density difference of the crystalline and amorphous regions. Taking the density difference between crystalline and amorphous regions $(\rho_c - \rho_a) = 0.143 \text{ g}/\text{cm}^3$ [15] based on an amorphous density $\rho_a = 0.854$, we have $(\eta_c - \eta_a) = (16/28) (\rho_c - \rho_a) = 8.17 \times 10^{-2} \text{ mol electron}/\text{cm}^3$ or $49.2 \text{ electrons}/\text{nm}^3$. Then $Q = 2421 (X_c X_a)$ and a value of $Q = 304$ could give a possible pair of values of X_c (or X_a) as 0.15 or 0.85. It is reasonable to choose $X_c = 0.85$. The base line value $-A$ is estimated by the relation $A/(A+Q) = X_a^{[12]}$ for this case of $X_c > 0.5$, which gives $A = 54$. The initial straight portion of $K(z)$ cuts the base line $K = -54$ at $z_1 = l_a = 4.8$ nm, and thus $l_c = 41 - 4.8 = 36$ nm and a linear crystallinity of $l_c/L = 36/41 = 0.88$. The presence of a crystalline region of high l_c and high crystallinity probably corresponds to the "strained crystalline region" of Phuong-Nguyen *et al.* [8] (sample used GUR of $M_w = 1.5 \times 10^6$), which melts only above 160°C and at a very slow rate of heating ($< 0.2 \text{ K}/\text{min}$). The crystallinity value 0.69 based on ΔH_m from DSC melting peak at 143°C (10 K/min) does not include this high melting crystalline regions. Thus, the crystalline state of the nascent UHPE sample B shows a long period $L = 41$ nm with crystalline regions of heterogeneous chain stem lengths $l_c \approx 30$ nm from X_c (DSC), containing a portion of the highest crystalline regions with a chain stem length $l_c = 36$ nm. This macromolecular condensed state is not really a fully extended chain crystalline state yet, which should have a value of $l_c > 10^4$ nm. The most convincing evidence for the extended chain state of nascent UHPE powder lies in the following experimental fact. When the powder of sample B was heated above its melting temperature, the melt remained birefringent although significantly weaker than the birefringence of the powder before melting, so that it appeared bright in the POM with crossed polars as shown in Fig. 6. The melt became optically isotropic only when it was heated above 180°C , presumably accompanied by degradation. In the absence of degradation the isotropization temperature may be well above 300°C [5]. Optical anisotropy was present even in liquid *n*-alkanes of 12–36 carbon atoms and the temperature of isotropization was found to be around $210\text{--}230^\circ\text{C}$ [16]. This optical anisotropy seems to have its origin in local nematic interactions of the chain segments longer than 8–9 carbon atoms, while the chains of C_{16} and C_{36} alkanes were not fully extended. It is reasonable to assume that when the crystalline chain stems melt down they form nematic domains of *ca.* 30 nm size in the UHPE melt.

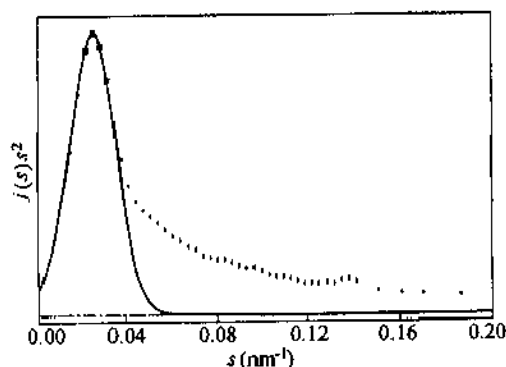


Fig. 4 $j(s)s^2$ versus s plot of the SAXS data, j being the scattered X-ray intensity

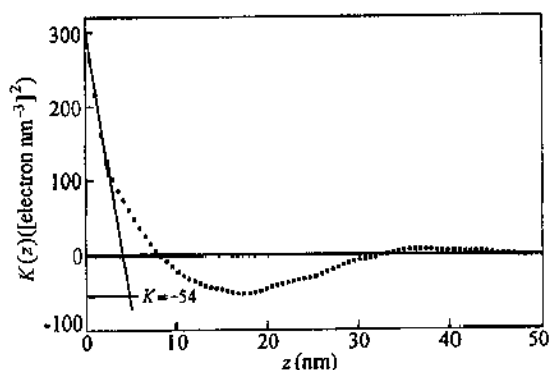


Fig. 5 One dimensional correlation function of SAXS of the sample B (nascent powder)

The above discussion means that the melt from nascent UHPE is in a nematic rubbery state with a nematic to isotropic transition temperature $T_{N \rightarrow I} > 300^\circ\text{C}$. As the chains in the nematic state have a preferred direction of

orientation parallel to each other, they do not interpenetrate, and these nematic nanodomains correspond to cohesional entanglements of longer chain segments, and consequently the melt behaves as a network. This is the reason, besides its ultra high molar mass, why an UHPE melt does not flow like the melt of an ordinary crystalline polymer, and it behaves like a rubber and can be easily stretched. Significant increase of birefringence was observed when the melt on a microscope slide was pressed by a cover glass^[5] at temperatures $< 220^{\circ}\text{C}$ also indicates a nematic rubbery state. Above 220°C the melt exhibited anisotropy without being pressed by a cover glass, although the birefringence was much decreased^[5] this probably means a transition from an anisotropic rubbery state to a weakly anisotropic fluid state, as the isotropic temperature may be above 300°C . Figure 7 shows the microphotograph of a film of sample B, compression molded at 130°C and quenched in ice-water, when it was heated to 150°C on a hot stage of a POM. The boundaries of the powder granules can be clearly seen (i.e. no flow resulted) with birefringent center part of the granules showing winding microfibrillar morphology. Thus we arrive at the conclusion that the nascent UHPE powder consists of fully extended chains of heterogeneous crystalline order. Apart from a small contribution of highly crystalline regions of $l_c \approx 36\text{ nm}$, the nascent state contains mainly crystalline regions with crystalline chain stem length of *ca.* 30 nm (sample B), which are interlaced by relaxed parallel chains as the amorphous regions of *ca.* 10 nm thickness in the direction of crystalline chain stems. This leads to a nematic melt on melting. That UHPE melt is capable of existing a nematic state was first mentioned by Chen and Jin^[9]. When they melt-stretched a film of 0.5 mm thickness compression molded at 200°C under a pressure of 9.8 MPa, a band texture was observed after being cooled to ambient temperature, which is typical for a main-chain nematic polymer^[17]. The macromolecular condensed state of nascent UHPE is therefore a rare case of essentially non-interpenetrating multi-chain condensed state. Only above 220°C the chains may start to interpenetrate each other, but it might take a considerable time to reach complete interpenetration of chains because of the ultra high molar mass. Before one is sure of no significant degradation of PE chain at such temperatures, it is difficult to estimate the relaxation time needed for interchain penetration. That is the reason why the nascent UHPE recrystallized after melting below 180°C , although T_m drops to 132°C or lower, it can be restored by annealing at $120\text{--}130^{\circ}\text{C}$. It also explains the results of Table I, where the melting of nascent UHPE at $150\text{--}170^{\circ}\text{C}$ for 5 min resulted in the same nematic melt. Even melting at 200°C for 5 min gave closely similar results, and the subsequent recrystallization on rapid cooling is the crystallization of UHPE chains from a nematic state. The value of T_m is apparently related to the crystalline chain stem length l_c and the degree of crystallinity X_c . Annealing below T_m will certainly lead to an increase of both l_c and X_c . Melting of extended chain crystalline regions to a nematic melt will have a smaller entropy change of melting, ΔS_m , than melting to a melt of interpenetrating chains. This is also a factor leading to a higher T_m .

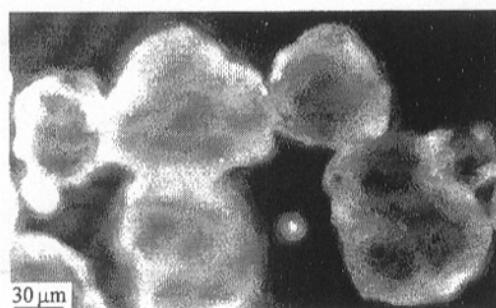


Fig. 6 POM micrograph of the sample B melted at 150°C , antioxidant added

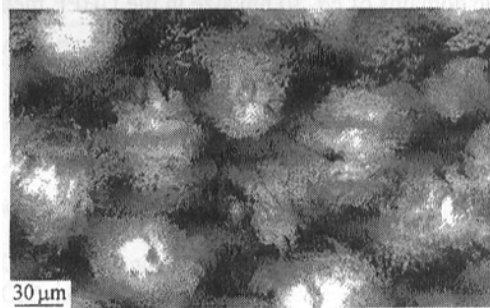


Fig. 7 POM micrograph of the sample B compression molded at 130°C and quenched, and then heated on the hot stage of the microscope to 150°C

CONCLUSION

The nascent UHPE powder is a multi-chain condensed state of non-interpenetrating chains, involving extended chains of crystalline order of chain stem length of *ca.* 30 nm interlaced by amorphous layers of relaxed parallel

chains. After melting of the crystalline layers the nascent UHPE powder changes to a nematic rubbery state, which becomes a weakly anisotropic fluid state above 220°C and has a $T_{N \rightarrow I} > 300^\circ\text{C}$. Because of the ultra high molar mass of the chains the relaxation from the state of non-interpenetrated chains to interpenetrating chains in the fluid state would be very slow. Hot compression molding of nascent UHPE powder at 130°C for 2 h retains the molecular chain condensed state of the nascent powder. The recrystallized UHPE after melting of the nascent powder followed by cooling to ambient temperature shows a drop of peak melting temperature T_m by around 10 K in its heating up DSC curve, which has its origin in the decrease of both crystalline stem length and degree of crystallinity on recrystallization. It could therefore be restored by annealing at 120~130°C to a molecular chain condensed state close to that of the nascent state.

Acknowledgements The authors would like to express their thanks to Professor Shangan Lin, Institute of Polymer Science, Zhongshan University, Guangzhou, for the sample A used; to Professor G.R. Strobl, Faculty of Physics, University of Freiburg, Germany, for the use of SAXS equipments and to Mrs. B. Heck for help in SAXS measurements and valuable discussions.

REFERENCES

- 1 Wunderlich, B., Hellmuth, E., Jaffe, M., Liberti, F., Rankin, J. and Koll, Z. Z., *Polym.*, 1965, 204: 125
- 2 Chanzy, H., Day, A. and Marchessault, R.H., *Polymer*, 1967, 8: 567
- 3 Wegner, G., Munoz-Escalona, A. and Fischer, E.W., *Makromol. Chem. Suppl.*, 1975, 1: 521
- 4 Smith, P., Chanzy, H.D. and Rotzinger, B.P., *J. Mater. Sci.*, 1987, 22: 523
- 5 Zachariades, A.E. and Logan, J.A., *J. Polym. Sci.*, 1983, 21: 821
- 6 Wang, X.-Y. and Salovey, R., *J. Appl. Polym. Sci.*, 1987, 34: 593
- 7 Wang, X.-Y., Li, S.-Y. and Salovey, R., *J. Appl. Polym. Sci.*, 1988, 35: 2165
- 8 Phuong-Nguyen, H. and Delmar, G., *Macromolecules*, 1992, 25: 408
- 9 Chen, S. and Jin, Y., *Polym. Mater. Sci. Eng.* (in Chinese), 1993, 9(2): 81
- 10 Zhu, Q.R., Hong, K.L., Ji, L.Q., Qi, R.R.R., Zhou, G.E., Song, M.S. and Wong, Y.W., *J. Polym. Sci. Polym. Phys. Ed.*, 1995, 33: 73
- 11 Strobl, G.R., *Acta Cryst.*, 1970, A26: 367
- 12 Strobl, G.R. and Schneider, M., *J. Polym. Sci. Polym. Phys. Ed.*, 1980, 18: 1343
- 13 Wunderlich, B. and Cormier, C.M., *J. Polym. Sci. Polym. Phys. Ed.*, 1967, 5: 987
- 14 Fischer, E.W., Hinrichsen, G. and Koll, Z.Z., *Polym.*, 1971, 247: 858
- 15 Wunderlich, B., "Macromolecular Physics Vol. 1. Crystal Structure, Morphology, Defects", Academic Press, New York, 1973, p.388
- 16 Fischer, E.W., Strobl, G.R., Dettenmaier, M., Stamm, M. and Steidle, N., *Faraday Discussion*, 1979, 68: 26
- 17 Qian, R. and Chen, S., *Makromol. Chem. Macromol. Symp.*, 1992, 53: 345